#### (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

## (19) World Intellectual Property Organization International Bureau





## (43) International Publication Date 11 April 2002 (11.04.2002)

#### **PCT**

## (10) International Publication Number WO 02/28186 A2

(51) International Patent Classification<sup>7</sup>: A01N 53/00 // (A01N 53/00, 61:00)

(21) International Application Number: PCT/US01/42444

(22) International Filing Date: 2 October 2001 (02.10.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/238,485 09/968,175 6 October 2000 (06.10.2000) US 1 October 2001 (01.10.2001) US

(71) Applicant (for all designated States except US): MON-SANTO TECHNOLOGY, LLC [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ASRAR, Jawed [US/US]; 14949 Royal Brook, Chesterfield, MO 63017 (US). KOHN, Frank, C. [US/US]; 12532 Larkwood Drive, St. Louis, MO 63146 (US).

(74) Agent: NELSON MULLINS RILEY & SCARBOR-OUGH; Keenan Building, Third Floor, 1330 Lady Street, Columbia, SC 29201 (US). (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

 without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## ζ,

#### (54) Title: SEED TREATMENT WITH COMBINATIONS OF INSECTICIDES

(57) Abstract: A method of preventing damage to the seed and/or shoots and foliage of a plant by a pest includes treating the seed from which the plant grows with a composition that includes a combination of at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. It is preferred that when the other insecticide is an oxadiazine derivative, the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin. The treatment is applied to the unsown seed. In another embodiment, the seed is a transgenic seed having at least one heterologous gene encoding for the expression of a protein having pesticidal activity against a first pest and the composition has activity against at least one second pest. Treated seeds are also provided.

# SEED TREATMENT WITH COMBINATIONS OF INSECTICIDES

CROSS REFERENCE TO RELATED PATENTS AND PATENT APPLICATIONS

5

This application is a non-provisional of U.S. Provisional Patent Application Serial No. 60/238,485, filed October 6, 2000, and claims priority thereto.

#### BACKGROUND OF THE INVENTION

### (1) Field of the Invention

10

This invention relates generally to the control of plant pests and more particularly to the provision of protection against insect damage to seeds and plant parts by the treatment of plant seeds with combinations of pesticides.

#### (2) Description of the Related Art

15

20

The control of insects and related arthropods is of extreme importance to the agricultural industry. Every year, these pests destroy an estimated 15% of agricultural crops in the United States and even more than that in developing countries. Some of this damage occurs in the soil when plant pathogens, insects and other such soil borne pests attack the seed after planting. Much of the rest of the damage is caused by rootworms; plant pathogens that feed upon or otherwise damage the plant roots; and by cutworms, European corn borers, and other pests that feed upon or damage the above ground parts of the plant. General descriptions of the type and mechanisms of attack of pests on agricultural crops are provided by, for example, Metcalf, in Destructive and Useful Insects, (1962); and Agrios, in Plant Pathology, 3rd Ed., Academic Press (1988).

25

The period during germination of the seed, sprouting and initial growth of the plant is particularly critical because the roots and shoots of the growing plant are small and even a small amount of damage can kill the entire plant. Moreover, some natural plant defenses are not fully developed at this stage and the plant is vulnerable to attack. Not surprisingly, the control of pests that attack the seed and the above

30

WO 02/28186

5

10

15

20

25

30

ground plant parts during this early stage of plant growth is a well developed area of agriculture.

Currently, the control of pests that attack post emergent crops primarily involves the application of synthetic organic pesticides to the soil, or to the growing plants by foliar spraying. Because of concern about the impact of chemical pesticides on public health and the environment, there has been much effort to reduce the amount of chemical pesticides that are used. A significant portion of this effort has been expended in developing transgenic crops engineered to express insect toxicants from microorganisms. For example, U.S. Patent No. 5,877,012 to Estruch et al. discloses the cloning and expression of proteins from such organisms as Bacillus. Pseudomonas, Clavibacter and Rhizobium into plants to obtain transgenic plants with resistance to such pests as black cutworms, armyworms, several borers and other insect pests. Publication WO/EP97/07089 by Privalle et al. teaches the transformation of monocotyledons, such as corn, with a recombinant DNA sequence encoding peroxidase for the protection of the plant from feeding by corn borers, earworms and cutworms. Jansens et al., in Crop Sci., 37(5):1616 - 1624 (1997), reported the production of transgenic corn containing a gene encoding a crystalline protein from Bacillus thuringiensis that controlled both generations of the European corn borer. U. S. Patent Nos. 5,625,136 and 5,859,336 to Koziel et al. reported that the transformation of corn with a gene from B. thuringiensis that encoded for delta-endotoxins provided the transgenic corn with improved resistance to European corn borer.

A comprehensive report of field trials of transgenic corn that expresses an insecticidal protein from *B. thuringiensis* has been provided by Armstrong *et al.*, in *Crop Science*, *35(2)*:550 - 557 (1995).

At the present state of plant cellular engineering, however, transgenic crops are typically resistant only to specific pests for that crop, *e.g.*, transgenic corn expressing a *Bt* toxin against the corn

rootworm. It is frequently necessary to apply synthetic pesticides to such transgenic plants to control damage by other pests.

5

10

15

20

25

30

Insecticides such as synthetic pyrethroids, organophosphates and carbamates; fungicides such as azoles and anilopyrimidines; and acaricides such as pyrazoles; and the like, are very effective against certain above ground plant pests when applied at the proper time and with proper procedures. Appropriate pesticides may be applied at the time of planting as surface bands, "T"-bands, or in-furrow, but these applications require the additional operation of applying the pesticide at the same time as the seeds are being sown. This complicates the planting operation and the additional equipment required for pesticide application is costly to purchase and requires maintenance and attention during use. Moreover, care must be taken to incorporate the pesticides properly into the topmost soil layer for optimal activity. (See, for example, the application requirements and precautions for use of tefluthrin that are described in the brochure titled *Force 3G Insecticide*, published by Zeneca Ag Products, Wilmington, DE (1998)).

The activity of pesticides that have been applied as in-furrow applications at the time of sowing is usually directed to the protection of the seed or the roots of the plant. Some protection against above ground pests such as corn borers has been reported, however, for such treatments with insecticides known to be systemic. Keaster and Fairchild, *J. Econ. Entomol.*, 61(2):367 - 369 (1968). Since such pesticide chemicals are complex molecules that are expensive to produce, purchase and use, it is desirable that their activity is not diluted or lost by migration away from the desired site of action by moisture seepage or by vaporization.

After the plant has emerged from the soil, foliar spraying of pesticides is most often used to control those pests that attach the shoots and foliage of the plant. However, a foliar spray must be applied at a certain time that coincides with the presence and activity of the pest in order to have the most beneficial effect. Application at this time may be difficult or impossible if, for example, weather conditions

10

15

20

25

30

limit access to the field. Moreover, the plants must be monitored closely to observe early signs of pest activity in order to apply the pesticide at a time when the pests are most vulnerable.

Synthetic pyrethroids have been found to give excellent control of pests of the order of Lepidoptera, such as cutworms, when applied as foliar spray or as surface-incorporated granules at the time of planting. However, since this class of insecticides has very high toxicity to fish, for example, great care must be taken to limit the runoff of the insecticide from either granules or spray into surface waters. Moreover, any foliar spraying must be done at times when there is little wind, and then only with proper equipment that is carefully monitored during use.

It has also been found in some cases with particular pesticides and application techniques that when two or more of such pesticides are used in particular combination greater efficacy results than when any one of such pesticides is used alone. Such benefits of combining pesticides has been reported for combinations of phosmet with diflubenzuron (U.S. Patent No. 4,382,927); O-ethyl-O-[4-(methylthio)-phenyl]-S-propyl phosphodithioate and N'-(4-chloro-o-tolyl)-N,N-dimethylformamidine (U.S. Patent No. 4,053,595); bacillus thuringiensis and chlordimeform (U.S. Patent No. 3,937,813); decamethrine and dichlorvos with propoxur, if desired, (U.S. Patent No. 4,863,909); fenvalerate and phosmet (U.S. Patent No. 4,263,287); and phosalone and malathion (U.S. Patent No. 4.064,237). However, each of these combinations was applied directly to the growing plant as described above in the form of sprays or dusts, or applied to the soil around the plant in the form of, for example, granules.

WO9740692 discloses combinations of any one of several oxadiazine derivatives with one of a long list of other insecticides. Although the application mentions that the combinations can be applied to plant propagation material for its protection, as well as to plant shoots and leaves, no examples are provided to demonstrate that any one of the combinations listed is actually efficacious. More pesticide

combinations are described in U.S. Patent Nos. 4,415,561, 5,385,926, 5,972,941 and 5,952,358. However, in the existing art, little or no guidance has been found as methods for predicting which combinations of pesticides will result in such unexpectedly superior efficacy and which combinations will not.

10

5

15

20

25

30

The control of pests by applying insecticides directly to plant seed is well known. For example, U.S. Patent No. 5,696,144 discloses that the European corn borer caused less feeding damage to corn plants grown from seed treated with a 1-arylpyrazole compound at a rate of 500 g per quintal of seed than control plants grown from untreated seed. In addition, U.S. Patent No. 5,876,739 to Turnblad et al. (and its parent, U. S. Patent No. 5,849,320) disclose a method for controlling soil-borne insects which involves treating seeds with a coating containing one or more polymeric binders and an insecticide. This reference provides a list of insecticides that it identifies as candidates for use in this coating and also names a number of potential target insects. However, while the 5,876,739 patent states that treating corn seed with a coating containing a particular insecticide protects corn roots from damage by the corn rootworm, it does not indicate or otherwise suggest that treatment of corn seed with any particular combinations of insecticides provides the seed or the plant with

Thus, although the art of protecting the shoots and foliage -- as well as the seed and roots -- of a plant from damage by pests has been advancing rapidly, several problems still remain. For example, it would be useful to provide a method for the control of pest damage to shoots and foliage of plants without the requirement of applying a pesticide at the time of sowing the seed, either as a surface incorporated band, or in-furrow, for example, or requiring a later field application of a pesticide during plant growth. It would also be useful if the method for pest control reduced the amount of pesticide that was required to provide a certain level of protection to the plant. Furthermore, it would be useful if such a method could be coupled with the biopesticidal

synergistic protection, or with any other unexpected advantage.

activity of transgenic plants, or with the insecticidal activity of other active materials to provide a broader scope of protection than is provided by the transgenic elements, or the insecticidal actives alone. SUMMARY OF THE INVENTION

5

10

Briefly, therefore, the present invention is directed to a novel method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating the unsown seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. It is preferred that when the other insecticide is an oxadizine derivative, the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin. Seeds that have been treated by this method are also provided.

20

25

15

The invention is also directed to a novel composition for the treatment of unsown seed comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. It is preferred that when the other insecticide is an oxadizine derivative, the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

30

The invention is also directed to a novel method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating the unsown seed with a composition comprising a nitroguanidine and at least one other

10

15

20

25

30

7

insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. Seeds that have been treated by this method are also provided.

The invention is also directed to a novel composition for treatment of unsown seed, the composition comprising a nitroguanidine and at least one other insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.

The invention is also directed to a novel seed that is protected against multiple pests comprising a seed having at least one heterologous gene encoding for the expression of a protein that is active against a first pest and, in addition, having adhered thereto a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate, where the composition is present in an amount effective to provide protection to the shoots and foliage of the plant against damage by at least one second pest.

The invention is also directed to a novel method for treating an unsown seed to prevent damage by a pest to the seed and/or shoots and foliage of a plant grown from the seed, the method comprising contacting the unsown seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate, provided that when the other insecticide is an oxadizine derivative, the pyrethroid is

selected from the group consisting of taufluvalinate, flumethrin, transcyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

5

10

Among the advantages found to be achieved by the present invention, therefore, may be noted the provision of a method for the control of pest damage to seeds and/or shoots and foliage of plants without the requirement of applying a pesticide at the time of sowing the seed, either as a surface incorporated band, or in-furrow, for example, or requiring a later field application of a pesticide during plant growth; the provision of a method for pest control that reduces the amount of pesticide that is required for the provision of a certain level of protection to the plant; and the provision of method that can be coupled with the biopesticidal activity of transgenic plants to selectively broaden the scope of protection that is provided for the shoots and foliage of the transgenic.

15

#### DETAILED DESCRIPTION OF THE PREFFERED EMBODIMENTS

20

In accordance with the present invention, it has been discovered that treatment of unsown plant seeds with a composition that includes a specific combination of insecticides not only protects the seeds themselves, but -- surprisingly -- also provides post-emergent control of pests that feed on or otherwise damage the shoots and/or foliage of the plant. The combination of insecticides that has been found to achieve such results is a combination of a pyrethrin or synthetic pyrethroid as one component, and with another component comprising one or more of certain other insecticides selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, such as imidacloprid, acetamiprid, and nitenpyram; a nitroguanidine; a pyrrol, such as chlorfenapyr; a pyrazole, such as tebufenpyrad; a diacylhydrazine, such as tebufenozide, methoxyfenozide, and halofenozide; a triazole, such as triazamate; a biological/fermentation product, such as avermectin and spinosad; a phenyl pyrazole, such as fipronil; an organophosphate, such as acephate, fenamiphos, diazinon,

30

25

chlorpyrifos, chlorpyrifon-methyl and malathion; and a carbamate, such as carbaryl, aldicarb, carbofuran, thiodicarb and oxamyl. It is preferred, however, that if the other insecticide is an oxadiazine derivative, the pyrethroid should be selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

In preferred embodiments, the combination of the insecticides provides unexpectedly superior protection in that the combination of the insecticides provides a level of protection to the seed and/or the plant that is superior to the level of protection that -- based on the current state of the art -- would be predicted from the protection provided by the individual components applied separately. This synergistic activity reduces the total amount of pesticide that is required to provide a certain level of protection. In addition to being more economical to use, the ability to use a reduced amount of pesticide for a given level of protection is advantageous in that seed treatments with reduced amounts of insecticides are less phytotoxic to the seed than when the insecticides are used separately.

Another advantage of the novel treatment is that it can be used with transgenic seeds of the type having a heterologous gene encoding for the expression of a pesticidal protein in the transgenic plant that grows from the seed. Treating such a seed with a pesticide provides the ability to protect against one pest with the transgenic trait and to provide surprisingly enhanced protection against the same pest, and/or to protect against other pests with the subject combination of

As used herein, the terms "pesticidal effect" and "pesticidal activity" mean any direct or indirect action on the target pest that results in reduced feeding damage on the seeds, roots, shoots and foliage of plants grown from treated seeds as compared to plants grown from untreated seeds. The terms "active against a (first or second) pest", also have the same meaning. Such direct or indirect

20

15

5

10

25

30

insecticides.

actions include inducing death of the pest, repelling the pest from the plant seeds, roots, shoots and/or foliage, inhibiting feeding of the pest on, or the laying of its eggs on, the plant seeds, roots, shoots and/or foliage, and inhibiting or preventing reproduction of the pest. The term "insecticidal activity" has the same meaning as pesticidal activity, except it is limited to those instances where the pest is an insect. When the term "pesticide" is used herein, it is not meant to include pesticides that are produced by the particular seed or the plant that grows from the particular seed that is treated with the pesticide.

10

15

5

As used herein, the "shoots and foliage" of a plant are to be understood to be the shoots, stems, branches, leaves and other appendages of the stems and branches of the plant after the seed has sprouted, but not including the roots of the plant. It is preferable that the shoots and foliage of a plant be understood to be those non-root parts of the plant that have grown from the seed and are located a distance of at least one inch away from the seed from which they emerged (outside the region of the seed), and more preferably, to be the non-root parts of the plant that are at or above the surface of the soil. As used herein, the "region of the seed" is to be understood to be that region within about one inch of the seed.

20

Pesticides suitable for use in the invention include pyrethrins and synthetic pyrethroids; oxadizine derivatives; chloronicotinyls; nitroguanidine derivatives; triazoles; organophosphates; pyrrols; pyrazoles; phenyl pyrazoles; diacylhydrazines; biological/fermentation products; and carbamates. Further information about pesticides of the types listed above can be found in *The Pesticide Manual*, 11th Ed., C. D. S. Tomlin, Ed., British Crop Protection Council, Farnham, Surry, UK (1997).

30

25

Pyrethroids that are useful in the present composition include pyrethrins and synthetic pyrethroids. The pyrethrins that are preferred for use in the present method include, without limitation, 2-allyl-4-hydroxy-3-methyl-2-cyclopenten-1-one ester of 2,2-dimethyl-3-(2methyl-propenyl)-cyclopropane carboxylic acid, and/or (2-methyl-1-propenyl)-

WO 02/28186

2-methoxy-4-oxo-3-(2 propenyl)-2-cyclopenten-1-yl ester and mixtures of cis and trans isomers thereof (Chemical Abstracts Service Registry Number ("CAS RN") 8003-34-7).

Synthetic pyrethroids that are preferred for use in the present 5 invention include (s)-cyano(3-phenoxyphenyl)methyl 4-chloro alpha (Imethylethyl)benzeneacetate (fenvalerate; CAS RN 51630-58-1); (S)cyano (3-phenoxyphenyl) methyl (S)-4-chloro-alpha-(1-methylethyl) benzeneacetate (esfenvalerate; CAS RN 66230-04-4); (3phenoxyphenyl)-methyl(+)cis-trans-3-(2,2-dichoroethenyl)-2,2-10 dimethylcyclopropanecarboxylate (permethrin; CAS RN 52645-53-1); (±) alpha-cyano-(3-phenoxyphenyl) methyl(+)-cis,trans-3-(2,2dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylate (cypermethrin; CAS RN 52315-07-8); (beta-cypermethrin; CAS RN 65731-84-2); (theta cypermethrin: CAS RN 71697-59-1); S-cyano (3-phenoxyphenyl) 15 methyl (±) cis/trans 3-(2,2-dichloroethenyl) 2,2 dimethylcyclopropane carboxylate (zeta-cypermethrin; CAS RN 52315-07-8); (s)-alphacyano-3-phenoxybenzyl (IR,3R)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropanecarboxylate (deltamethrin; CAS RN 52918-63-5); alphacyano-3-phenoxybenzyl 2,2,3,3,-tetramethyl cyclopropoanecarboxylate 20 (fenpropathrin; CAS RN 64257-84-7); (RS)-alpha-cyano-3phenoxybenzyl(R)-2-[2-chloro-4-(trifluoromethyl)anilino]-3methylbutanoate (tau-fluvalinate; CAS RN 102851-06-9); (2,3,5,6tetrafluoro-4-methylphenyl)-methyl-(1 alpha, 3 alpha)-(Z)-(±)-3-(2chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate 25 (tefluthrin; CAS RN 79538-32-2); (±)-cyano (3-phenoxyphenyl) methyl (±)-4-(difluoromethoxy)-alpha-(1-methyl ethyl) benzeneacetate (flucythrinate; CAS RN 70124-77-5); cyano(4-fluoro-3phenoxyphenyl)methyl 3-[2-chloro-2-(4-chlorophenyl)ethenyl]-2,2dimethylcyclopropanecarboxylate (flumethrin; CAS RN 69770-45-2); 30 cyano(4-fluoro-3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2dimethyl-cyclopropanedarboxylate (cyfluthrin; CAS RN 68359-37-5); (beta cyfluthrin; CAS RN 68359-37-5); (transfluthrin; CAS RN 118712-89-3); (S)-alpha-cyano-3-phenoxybenzyl(Z)-(IR-cis)-2,2-dimethyl-3-[2-

PCT/US01/42444 WO 02/28186

(2,2,2-trifluoro-trifluoromethyl-ethoxycarbonyl)vinyl]cyclopropane carboxylate (acrinathrin; CAS RN 101007-06-1); (IR cis) S and (IS cis) R enantiomer isomer pair of alpha-cyano-3-phenoxybenzyl-3-(2,2dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (alpha-5 cypermethrin; CAS RN 67375-30-8); [IR,3S)3(1'RS)(1',2',2',2'tetrabromoethyl)]-2,2-dimethyl cyclopropanecarboxylic acid (s)-alphacyano-3-phenoxybenzyl ester (tralomethrin; CAS RN 66841-25-6); cvano-(3-phenoxyphenyl) methyl 2,2-dichloro-1- (4ethoxyphenyl)cyclopropane carboxylate (cycloprothrin; CAS RN 63935-10 38-6);  $[1\alpha, 3\alpha(Z)]$ -(±)-cyano-(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-cimethylcyclopropanecarboxylate (cyhalothrin; CAS RN 68085-85-8); [1 alpha (s), 3 alpha(z)]-cyano(3phenoxyphenyl) methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2dimethylcyclopropane carboxylate (lambda cyhalothrin; CAS RN 15 91465-08-6); (2-methyl [1,1'-biphenyl]-3-yl) methyl 3-(2-chloro-3,3,3trifluoro-1-propenyl)-2,2-dimethyl-cyclopropanecarboxylate (bifenthrin; CAS RN 82657-04-3); 5-1-benzyl-3-furylmethyl-d-cis(1R,3S,E)2,2dimethyl-3-(2-oxo,-2,2,4,5 tetrahydro thiophenylidenemethyl)cyclopropane carboxylate (kadethrin, RU15525; 20 CAS RN 58769-20-3); [5-(phenyl methyl)-3-furanyl]-3-furanyl 2,2dimethyl-3-(2-methyl-1-propenyl) cyclopropane carboxylate (resmethrin; CAS RN 10453-86-8); (1R-trans)-[5-(phenylmethyl)-3furanyl]methyl 2.2-dimethyl-3-(2-methyl-1propenyl)cyclopropanecarboxylate (bioresmethrin; CAS RN 28434-01-25 7); 3,4,5,6-tetra hydro-phthalimidomethyl-(IRS)-cis-transchrysanthemate (tetramethrin; CAS RN 7696-12-0); 3-phenoxybenzyld,l-cis,trans 2,2-dimethyl-3-(2-methylpropenyl) cyclopropane carboxylate (phenothrin; CAS RN 26002-80-2); (empenthrin; CAS RN 54406-48-3); (cyphenothrin; CAS RN 39515-40-7); (prallethrin; CAS 30 RN 23031-36-9); (imiprothrin; CAS RN 72963-72-5); (RS)-3-allyl-2methyl-4-oxcyclopent-2-enyl-(1A,3R; 1R,3S)-2,2-dimethyl-3- (2methylprop-1-enyl) cyclopropane carboxylate (allethrin; CAS RN 584-

79-2); (bioallethrin; CAS RN 584-79-2); and (ZXI8901; CAS RN

10

15

20

25

30

160791-64-0). It is believed that mixtures of one or more of the aforementioned synthetic pyrethroids can also be used in the present invention.

In one embodiment of the present invention, particularly preferred synthetic pyrethroids are tefluthrin, lambda cyhalothrin, bifenthrin, permethrin and cyfluthrin. Even more preferred synthetic pyrethroids are tefluthrin and lambda cyhalothrin.

In another embodiment of the invention — where an oxadiazine derivative is used as one of the combination of insecticides — the preferred synthetic pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

The pyrethrins and synthetic pyrethroids that are useful in the present compositions can be of any grade or purity that pass in the trade as pyrethrins and synthetic pyrethroids. Other materials that accompany the pyrethrins and synthetic pyrethroids in commercial preparations as impurities can be tolerated in the subject compositions, as long as such other materials do not destabilize the composition or significantly reduce or destroy the activity of any of the insecticide components against the target pest. One of ordinary skill in the art of the production of insecticides can readily identify those impurities that can be tolerated and those that cannot.

Insecticides that are oxadiazine derivatives are useful as one of the components of the subject composition. Oxadizine derivatives that are preferred for use in the present invention include 5-(2-chloropyrid-5-ylmethyl)-3-methyl-4-nitroiminoperhydro-1,3,5-oxadiazine; 3-methyl-4-nitroimino-5-(1-oxido-3-pyridinomethyl) perhydro-1,3,5-oxadiazine; 5-(2-chloro-1-oxido-5-pyridiniomethyl)-3-methyl-4-nitroiminoperhydro-1,3,5-oxidiazine; and 3-methyl-5-(2-methylpyrid-5-ylmethyl)-4-nitroiminoperhydro-1,3,5-oxadiazine.

Chloronicotinyl insecticides are also useful as one of the components of the subject composition. Chloronicotinyls that are

preferred for use in the subject composition include acetamiprid ((E)-N-[(6-chloro-3-pyridinyl)methyl]-N'-cyano-N-methyleneimidamide; CAS RN 135410-20-7); imidacloprid (1-[(6-chloro-3-pyridinyl)methol]-N-nitro-2-imidazolidinimime; CAS RN 138261-41-3); and nitenpyram (N-[(6-chloro-3-pyridinyl)methyl]-N-ethyl-N'-methyl-2-nitro-1,1-ethenediamine; CAS RN 120738-89-8).

Nitroguanidine insecticides are useful as one of the components of the present combination. Nitroguanidines that are preferred for use in the present invention include MTI 446 (nidinotefuran).

10

15

5

Pyrrols, pyrazoles and phenyl pyrazoles that are useful in the present composition include those that are described in U.S. Patent 5,952,358. Preferred pyrazoles include chlorfenapyr (4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethylpyrrole-3-carbonitrile; CAS RN 122453-73-0); fenpyroximate ((E)-1,1-dimethylethyl-4[[[[(1,3-dimethyl-5-phenoxy-1H-pyrazole-4-yl)methylene]amino]oxy]methyl]benzoate; CAS RN 111812-58-9); and tebufenpyrad (4-chloro-N[[4-1,1-dimethylethyl)phenyl]methyl]-3-ethyl-1-methyl-1H-pyrazole-5-carboxamide; CAS RN 119168-77-3). A preferred phenyl pyrazole is fipronil (5-amino-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(1R,S)-(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile; CAS RN 120068-37-3).

20

Diacylhydrazines that are useful in the present invention include halofenozide (4-chlorobenzoate-2-benzoyl-2-(1,1-dimethylethyl)-hydrazide; CAS RN 112226-61-6); methoxyfenozide (RH-2485; N-tert-butyl-N'-(3-methoxy-o-toluoyl)-3,5-xylohydrazide; CAS RN 161050-58-4); and tebufenozide (3,5-dimethylbenzoic acid 1-(1,1-dimethylethyl)-2,(4-ethylbenzoyl)hydrazide; CAS RN 112410-23-8).

30

25

Triazoles, such as amitrole (CAS RN 61-82-5) and triazamate are useful in the composition of the present invention. A preferred triazole is triazamate (ethyl [[1-[(dimethylamino)carbonyl]-3-(1,1-dimethylethyl)-1H-1,2,4-triazol-5-yl]thio]acetate; CAS RN 112143-82-5).

Biological/fermentation products, such as avermectin (abamectin; CAS RN 71751-41-2) and spinosad (XDE-105, CAS RN 131929-60-7) are useful in the present composition.

Organophosphate insecticides are also useful as one of the components of the composition of the present invention. Preferred organophophate insecticides include acephate (CAS RN 30560-19-1); chlorpyrifos (CAS RN 2921-88-2); chlorpyrifos-methyl (CAS RN 5598-13-0); diazinon (CAS RN 333-41-5); fenamiphos (CAS RN 22224-92-6); and malathion (CAS RN 121-75-5).

10

5

In addition, carbamate insecticides are useful in the subject composition. Preferred carbamate insecticides are aldicarb (CAS RN 116-06-3); carbaryl (CAS RN 63-25-2); carbofuran (CAS RN 1563-66-2); oxamyl (CAS RN 23135-22-0) and thiodicarb (CAS RN 59669-26-0).

15

When an insecticide is described herein, it is to be understood that the description is intended to include salt forms of the insecticide as well as any isomeric and/or tautomeric form of the insecticide that exhibits the same insecticidal activity as the form of the insecticide that is described.

20

25

30

One embodiment of this invention comprises treating a seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazole, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. The treatment is applied to the seed prior to sowing the seed so that the sowing operation is simplified. In this manner, seeds can be treated, for example, at a central location and then dispersed for planting. This permits the person who plants the seeds to avoid the handling and use of insecticides -- some of which can be toxic -- and to merely handle and plant the treated seeds in a manner that is conventional for regular untreated seeds. It is preferred, in some combinations that at least one of the pyrethroid and the other insecticide is a systemic insecticide.

In this embodiment, a seed can be treated with any one of the combinations of insecticides that are shown in Table 1.

Table 1: Combinations of pyrethroids and other non-pyrethroid insecticides that provide synergistic insecticidal activity<sup>a</sup>.

COMPOSITION	<b>PYRETHROID</b>	OTHER INSECTICIDE
NO.		
<u> </u>	lambda-cyhalothrin	acetamiprid
2	lambda-cyhalothrin	imidacloprid
2 3	lambda-cyhalothrin	nitenpyram
4	lambda-cyhalothrin	nidinotefuran
5	lambda-cyhalothrin	chlorfenapyr
6	lambda-cyhalothrin	fenpyroximate
7	lambda-cyhalothrin	tebufenpyrad
8	lambda-cyhalothrin	fipronil
9	lambda-cyhalothrin	tebufenozide
10	lambda-cyhalothrin	methoxyfenozide
11	lambda-cyhalothrin	halofenozide
12	lambda-cyhalothrin	triazamate
13	lambda-cyhalothrin	avermectin
14	lambda-cyhalothrin	spinosad
15	lambda-cyhalothrin	acephate
16	lambda-cyhalothrin	fenamiphos
17	lambda-cyhalothrin	diazinon
18	lambda-cyhalothrin	chlorpyrifos
19	lambda-cyhalothrin	chlorpyrifos-methyl
20	lambda-cyhalothrin	malathion
21	lambda-cyhalothrin	carbaryl
22	lambda-cyhalothrin	aldicarb
23	lambda-cyhalothrin	carbofuran
24	lambda-cyhalothrin	thiodicarb
25	lambda-cyhalothrin	oxamyl
26	tefluthrin	acetamiprid
27	tefluthrin	imidacloprid
28	tefluthrin	nitenpyram
29	tefluthrin	nidinotefuran
30	tefluthrin	chlorfenapyr
31	tefluthrin	fenpyroximate
32	tefluthrin	tebufenpyrad
33	tefluthrin	fipronil
34	tefluthrin	tebufenozide
35	tefluthrin	methoxyfenozide
36	tefluthrin	halofenozide
37	tefluthrin	triazamate
38	tefluthrin	avermectin

39	tefluthrin	spinosad
40	tefluthrin	acephate
41	tefluthrin	fenamiphos
42	tefluthrin	diazinon
43	tefluthrin	chlorpyrifos
44	tefluthrin	chlorpyrifos-methyl
4 <del>4</del> 45	tefluthrin	malathion
45 46		
	tefluthrin	carbaryl
47	tefluthrin	aldicarb
48	tefluthrin	carbofuran
49	tefluthrin	thiodicarb
50	tefluthrin	oxamyl
51	cyfluthrin	acetamiprid
52	cyfluthrin	imidacloprid
53	cyfluthrin	nitenpyram
54	cyfluthrin	nidinotefuran
55	cyfluthrin	chlorfenapyr
56	cyfluthrin	fenpyroximate
57	cyfluthrin	tebufenpyrad 、
58	cyfluthrin	fipronil
59	cyfluthrin	tebufenozide
60	cyfluthrin	methoxyfenozide
61	cyfluthrin	halofenozide
62	cyfluthrin	triazamate
63	cyfluthrin	avermectin
64	cyfluthrin	spinosad
65	cyfluthrin	acephate
66	cyfluthrin	fenamiphos
67	cyfluthrin	diazinon
68	cyfluthrin	chlorpyrifos
69	cyfluthrin	chlorpyrifos-methyl
70	cyfluthrin	malathion
71	cyfluthrin	carbaryl
72	cyfluthrin	aldicarb
73	cyfluthrin	carbofuran
73 74	cyfluthrin	thiodicarb
7 <del>4</del> 75	cyfluthrin	
75	Cynuumm	oxamyl
76	bifenthrin	acetamiprid
77	bifenthrin	imidacloprid
78	bifenthrin	nitenpyram
79	bifenthrin	nidinotefuran
80	bifenthrin	chlorfenapyr
81	bifenthrin	fenpyroximate
82	bifenthrin	tebufenpyrad
83	bifenthrin	fipronil
84	bifenthrin	tebufenozide
85	bifenthrin	methoxyfenozide

WO 02/28186 PCT/US01/42444

86	bifenthrin	halofenozide
87	bifenthrin	triazamate
88	bifenthrin	avermectin
89	bifenthrin	spinosad
90	bifenthrin	acephate
91	bifenthrin	fenamiphos
92	bifenthrin	diazinon
93	bifenthrin	chlorpyrifos
94	bifenthrin	chlorpyrifos-methyl
95	bifenthrin	malathion
96	bifenthrin	carbaryl
97	bifenthrin	aldicarb
98	bifenthrin	carbofuran
99	bifenthrin	thiodicarb
100	bifenthrin	
100	bliendinii	oxamyl
101	fenvalerate	acetamiprid
102	fenvalerate	imidacloprid
103	fenvalerate	nitenpyram
104	fenvalerate	nidinotefuran
105	fenvalerate	chlorfenapyr
106	fenvalerate	fenpyroximate
107	fenvalerate	tebufenpyrad
108	fenvalerate	fipronil
109	fenvalerate	tebufenozide
110	fenvalerate	methoxyfenozide
111	fenvalerate	halofenozide
112	fenvalerate	triazamate
113	fenvalerate	avermectin
114	fenvalerate	spinosad
115	fenvalerate	acephate
116	fenvalerate	fenamiphos
117	fenvalerate	diazinon
118	fenvalerate	chlorpyrifos
119	fenvalerate	chlorpyrifos-methyl
120	fenvalerate	malathion
121	fenvalerate	carbaryl
122	fenvalerate	aldicarb
123	fenvalerate	carbofuran
124	fenvalerate	thiodicarb
125	fenvalerate	oxamyl
126	esfenvalerate	a a ata main wid
127		acetamiprid
	esfenvalerate	imidacloprid
128	esfenvalerate	nitenpyram
129	esfenvalerate	nidinotefuran
130	esfenvalerate	chlorfenapyr
131	esfenvalerate	fenpyroximate
132	esfenvalerate	tebufenpyrad

133	esfenvalerate	fipronil
134	esfenvalerate	tebufenozide
135	esfenvalerate	methoxyfenozide
136	esfenvalerate	halofenozide
137	esfenvalerate	triazamate
138	esfenvalerate	avermectin
139	esfenvalerate	spinosad
140	esfenvalerate	acephate
141	esfenvalerate	fenamiphos
141	esfenvalerate	diazinon
142	esfenvalerate	chlorpyrifos
144	esfenvalerate	chlorpyrifos-methyl
144	esfenvalerate	malathion
145	esfenvalerate	carbaryl
	esfenvalerate	aldicarb
147		carbofuran
148	esfenvalerate esfenvalerate	thiodicarb
149		
150	esfenvalerate	oxamyl
151	permethrin	acetamiprid
152	permethrin	imidacloprid
153	permethrin	nitenpyram
154	permethrin	nidinotefuran
155	permethrin	chlorfenapyr
156	permethrin	fenpyroximate
157	permethrin	tebufenpyrad
158	permethrin	fipronil
159	permethrin	tebufenozide
160	permethrin	methoxyfenozide
161	permethrin	halofenozide
162	permethrin	triazamate
163	permethrin	avermectin
164	permethrin	spinosad
165	permethrin	acephate
166	permethrin	fenamiphos
167	permethrin	diazinon
168	permethrin	chlorpyrifos
169	permethrin	chlorpyrifos-methyl
170	permethrin	malathion
171	permethrin	carbaryl
172	permethrin	aldicarb
173	permethrin	carbofuran
174	permethrin	thiodicarb
175	permethrin	oxamyl
176	cypermethrin	acetamiprid
177	cypermethrin	imidacloprid
178	cypermethrin	nitenpyram
179	cypermethrin	nidinotefuran
113	cypermeann	Humotolulan

180	cypermethrin	chlorfenapyr
181	cypermethrin	fenpyroximate
182	cypermethrin	tebufenpyrad
183	cypermethrin	fipronil
184	cypermethrin	tebufenozide
185	cypermethrin	methoxyfenozide
186		halofenozide
	cypermethrin	
187	cypermethrin	triazamate
188	cypermethrin	avermectin
189	cypermethrin	spinosad
190	cypermethrin	acephate
191	cypermethrin	fenamiphos
192	cypermethrin	diazinon
193	cypermethrin	chlorpyrifos
194	cypermethrin	chlorpyrifos-methyl
195	cypermethrin	malathion
196	cypermethrin	carbaryl
197	cypermethrin	aldicarb
198	cypermethrin	carbofuran
199	cypermethrin	thiodicarb
200	cypermethrin	oxamyl
201	beta-cypermethrin	acetamiprid
202	beta-cypermethrin	imidacloprid
203	beta-cypermethrin	nitenpyram
204	beta-cypermethrin	nidinotefuran
205	beta-cypermethrin	chlorfenapyr
206	beta-cypermethrin	fenpyroximate
207	beta-cypermethrin	tebufenpyrad
208	beta-cypermethrin	fipronil
209	beta-cypermethrin	tebufenozide
210	beta-cypermethrin	methoxyfenozide
211	beta-cypermethrin	halofenozide
212	beta-cypermethrin	triazamate
213	beta-cypermethrin	avermectin
214	beta-cypermethrin	spinosad
215	beta-cypermethrin	acephate
216	beta-cypermethrin	fenamiphos
217	beta-cypermethrin	diazinon
218	beta-cypermethrin	chlorpyrifos
219	beta-cypermethrin	chlorpyrifos-methyl
220	beta-cypermethrin	malathion
221	beta-cypermethrin	carbaryl
222	beta-cypermethrin	aldicarb
223	beta-cypermethrin	carbofuran
224	beta-cypermethrin	thiodicarb
225	beta-cypermethrin	oxamyl
226	theta-cypermethrin	acetamiprid
	meta oyponneumm	acctampna

WO 02/28186 PCT/US01/42444

227	theta-cypermethrin	imidacloprid
228	theta-cypermethrin	nitenpyram
229	theta-cypermethrin	nidinotefuran
230	theta-cypermethrin	chlorfenapyr
231	theta-cypermethrin	fenpyroximate
232	theta-cypermethrin	tebufenpyrad
233	theta-cypermethrin	fipronil
234	theta-cypermethrin	tebufenozide
235	theta-cypermethrin	methoxyfenozide
236	theta-cypermethrin	halofenozide
237	theta-cypermethrin	triazamate
238	theta-cypermethrin	avermectin
239	theta-cypermethrin	spinosad
240	theta-cypermethrin	acephate
241	theta-cypermethrin	fenamiphos
242	theta-cypermethrin	diazinon
243	theta-cypermethrin	chlorpyrifos
244	theta-cypermethrin	chlorpyrifos-methyl
245	theta-cypermethrin	malathion
246	theta-cypermethrin	carbaryl
247	theta-cypermethrin	aldicarb
248	theta-cypermethrin	carbofuran
249	theta-cypermethrin	thiodicarb
250	theta-cypermethrin	oxamyl
251	zota ovnormathrin	a a a ta main wid
252	zeta-cypermethrin	acetamiprid
253	zeta-cypermethrin zeta-cypermethrin	imidacloprid
254	zeta-cypermethrin	nitenpyram nidinotefuran
255	zeta-cypermethrin	chlorfenapyr
256	zeta-cypermethrin	fenpyroximate
257	zeta-cypermethrin	tebufenpyrad
258	zeta-cypermethrin	fipronil
259	zeta-cypermethrin	tebufenozide
260	zeta-cypermethrin	methoxyfenozide
261	zeta-cypermethrin	halofenozide
262	zeta-cypermethrin	triazamate
263	zeta-cypermethrin	avermectin
264	zeta-cypermethrin	spinosad
265	zeta-cypermethrin	acephate
266	zeta-cypermethrin	fenamiphos
267	zeta-cypermethrin	diazinon
268	zeta-cypermethrin	chlorpyrifos
269	zeta-cypermethrin	chlorpyrifos-methyl
270	zeta-cypermethrin	malathion
271	zeta-cypermethrin	carbaryl
272	zeta-cypermethrin	aldicarb
	20ta Oyporniculiii	ลเนเนสเม
Z 1 .)	• •	carhofuran
273 274	zeta-cypermethrin zeta-cypermethrin	carbofuran thiodicarb

275	zeta-cypermethrin	oxamyl
276	deltamethrin	acetamiprid
277	deltamethrin	imidacloprid
278	deltamethrin	nitenpyram
279	deltamethrin	nidinotefuran
280	deltamethrin	chlorfenapyr
281	deltamethrin	fenpyroximate
282	deltamethrin	tebufenpyrad
283	deltamethrin	fipronil
284	deltamethrin	tebufenozide
285	deltamethrin	methoxyfenozide
286	deltamethrin	halofenozide
287	deltamethrin	triazamate
288	deltamethrin	avermectin
289	deltamethrin	spinosad
299	deltamethrin	•
290	deltamethrin	acephate
291	deltamethrin	fenamiphos diazinon
	deltamethrin	
293		chlorpyrifos
294	deltamethrin deltamethrin	chlorpyrifos-methyl malathion
295		
296	deltamethrin	carbaryl
297	deltamethrin	aldicarb
298	deltamethrin	carbofuran
299	deltamethrin	thiodicarb
300	deltamethrin	oxamyl
301	fenpropathrin	acetamiprid
302	fenpropathrin	imidacloprid
303	fenpropathrin	nitenpyram
304	fenpropathrin	nidinotefuran
305	fenpropathrin	chlorfenapyr
306	fenpropathrin	fenpyroximate
307	fenpropathrin	tebufenpyrad
308	fenpropathrin	fipronil
309	fenpropathrin	tebufenozide
310	fenpropathrin	methoxyfenozide
311	fenpropathrin	halofenozide
312	fenpropathrin	triazamate
313	fenpropathrin	avermectin
314	fenpropathrin	spinosad
315	fenpropathrin	acephate
316	fenpropathrin	fenamiphos
317	fenpropathrin	diazinon
318	fenpropathrin	chlorpyrifos
319	fenpropathrin	chlorpyrifos-methyl
320	fenpropathrin	malathion
321	fenpropathrin	carbaryl
	, , ,	

322	fenpropathrin	aldicarb
323	fenpropathrin	carbofuran
324	fenpropathrin	thiodicarb
325	fenpropathrin	oxamyl
	• •	•
326	taufluvalinate .	acetamiprid
327	taufluvalinate	imidacloprid
328	taufluvalinate	nitenpyram
329	taufluvalinate	nidinotefuran
330	taufluvalinate	
		chlorfenapyr
331	taufluvalinate	fenpyroximate
332	taufluvalinate	tebufenpyrad
333	taufluvalinate	fipronil
334	taufluvalinate	tebufenozide
335	taufluvalinate	methoxyfenozide
336	taufluvalinate	halofenozide
337	taufluvalinate	triazamate
338	taufluvalinate	avermectin
339	taufluvalinate	spinosad
340	taufluvalinate	acephate
341	taufluvalinate	fenamiphos
342	taufluvalinate	diazinon
343	taufluvalinate	chlorpyrifos
344	taufluvalinate	chlorpyrifos-methyl
345	taufluvalinate	malathion
346	taufluvalinate	
		carbaryl
347	taufluvalinate	aldicarb
348	taufluvalinate	carbofuran
349	taufluvalinate	thiodicarb
350	taufluvalinate	oxamyl
351	flucythrinate	acetamiprid
352	flucythrinate	imidacloprid
353	flucythrinate	nitenpyram
354	flucythrinate	nidinotefuran
355	flucythrinate	chlorfenapyr
356	flucythrinate	fenpyroximate
357	flucythrinate	tebufenpyrad
358	flucythrinate	fipronil
359	flucythrinate	tebufenozide
360	flucythrinate	methoxyfenozide
361	flucythrinate	halofenozide
362	flucythrinate	triazamate
363	flucythrinate	avermectin
364		
	flucythrinate	spinosad
365	flucythrinate	acephate
366	flucythrinate	fenamiphos
367	flucythrinate	diazinon
368	flucythrinate	chlorpyrifos

369	flucythrinate	chlorpyrifos-methyl
370	flucythrinate	malathion
371	flucythrinate	carbaryl
372	flucythrinate	aldicarb
373	flucythrinate	carbofuran
	•	
374	flucythrinate	thiodicarb
375	flucythrinate	oxamyl
376	flumethrin	acetamiprid
377	flumethrin	imidacloprid
378	flumethrin	nitenpyram
379	flumethrin	nidinotefuran
380	flumethrin	chlorfenapyr
381	flumethrin	fenpyroximate
382	flumethrin	tebufenpyrad
383	flumethrin	fipronil
384	flumethrin	tebufenozide
385	flumethrin	methoxyfenozide
386	flumethrin	halofenozide
387	flumethrin	triazamate
388	flumethrin	avermectin
389	flumethrin	spinosad
390	flumethrin	acephate
391	flumethrin	fenamiphos
392	flumethrin	diazinon
393	flumethrin	
394	flumethrin	chlorpyrifos
	flumethrin	chlorpyrifos-methyl malathion
395		
396	flumethrin	carbaryl
397	flumethrin	aldicarb
398	flumethrin	carbofuran
399	flumethrin	thiodicarb
400	flumethrin	oxamyl
401	beta-cyfluthrin	acetamiprid
402	beta-cyfluthrin	imidacloprid
403	beta-cyfluthrin	nitenpyram
404	beta-cyfluthrin	nidinotefuran
405	beta-cyfluthrin	chlorfenapyr
406	beta-cyfluthrin	fenpyroximate
407	beta-cyfluthrin	tebufenpyrad
408	beta-cyfluthrin	fipronil
409	beta-cyfluthrin	tebufenozide
410	beta-cyfluthrin	methoxyfenozide
411	beta-cyfluthrin	halofenozide
412	beta-cyfluthrin	triazamate
413	beta-cyfluthrin	avermectin
414	beta-cyfluthrin	spinosad
415	beta-cyfluthrin	acephate
•	bota dynatiiii	acophate

WO 02/28186 PCT/US01/42444 25

416 417 418 419 420 421	beta-cyfluthrin beta-cyfluthrin beta-cyfluthrin beta-cyfluthrin beta-cyfluthrin	fenamiphos diazinon chlorpyrifos chlorpyrifos-methyl malathion carbaryl
422 423 424	beta-cyfluthrin beta-cyfluthrin beta-cyfluthrin	aldicarb carbofuran thiodicarb
425	beta-cyfluthrin	oxamyl
426 427	trans-cyfluthrin trans-cyfluthrin	acetamiprid imidacloprid
428	•	•
420 429	trans-cyfluthrin	nitenpyram nidinotefuran
430	trans-cyfluthrin	
430	trans-cyfluthrin	chlorfenapyr
431	trans-cyfluthrin	fenpyroximate
	trans-cyfluthrin	tebufenpyrad
433	trans-cyfluthrin	fipronil
434	trans-cyfluthrin	tebufenozide
435	trans-cyfluthrin	methoxyfenozide
436	trans-cyfluthrin	halofenozide
437	trans-cyfluthrin	triazamate
438	trans-cyfluthrin	avermectin
439	trans-cyfluthrin	spinosad
440	trans-cyfluthrin	acephate
441	trans-cyfluthrin	fenamiphos
442	trans-cyfluthrin	diazinon
443	trans-cyfluthrin	chlorpyrifos
444	trans-cyfluthrin	chlorpyrifos-methyl
445	trans-cyfluthrin	malathion
446	trans-cyfluthrin	carbaryl
447	trans-cyfluthrin	aldicarb
448	trans-cyfluthrin	carbofuran
449	trans-cyfluthrin	thiodicarb
450	trans-cyfluthrin	oxamyl
451	acrinathrin	acetamiprid
452	acrinathrin	imidacloprid
453	acrinathrin	nitenpyram
454	acrinathrin	nidinotefuran
455	acrinathrin	chlorfenapyr
456	acrinathrin	fenpyroximate
457	acrinathrin	tebufenpyrad
458	acrinathrin	fipronil
459	acrinathrin	tebufenozide
460	acrinathrin	methoxyfenozide
461	acrinathrin	halofenozide
462	acrinathrin	triazamate

WO 02/28186 PCT/US01/42444

463	acrinathrin	avermectin
464	acrinathrin	spinosad
465	acrinathrin	, acephate
466	acrinathrin	fenamiphos
467	acrinathrin	diazinon
468	acrinathrin	chlorpyrifos
469	acrinathrin	chlorpyrifos-methyl
470	acrinathrin	malathion
471	acrinathrin	carbaryl
472	acrinathrin	aldicarb
473	acrinathrin	carbofuran
474	acrinathrin	thiodicarb
474		
4/5	acrinathrin	oxamyl
476	alphacypermethrin	acetamiprid
477	alphacypermethrin	imidacloprid
478	alphacypermethrin	nitenpyram
479	alphacypermethrin	nidinotefuran
480	alphacypermethrin	chlorfenapyr
481	alphacypermethrin	fenpyroximate
482	alphacypermethrin	tebufenpyrad
483	alphacypermethrin	fipronil
484	alphacypermethrin	tebufenozide
485	alphacypermethrin	methoxyfenozide
486	alphacypermethrin	halofenozide
487	alphacypermethrin	triazamate
488	alphacypermethrin	avermectin
489	alphacypermethrin	spinosad
490	alphacypermethrin	acephate
491	alphacypermethrin	fenamiphos
492	alphacypermethrin	diazinon
493	alphacypermethrin	chlorpyrifos
494	alphacypermethrin	chlorpyrifos-methyl
495	alphacypermethrin	malathion
496	alphacypermethrin	carbaryl
497	alphacypermethrin	aldicarb
498	alphacypermethrin	carbofuran
499	alphacypermethrin	thiodicarb
500	alphacypermethrin	oxamyl
501	tralomethrin	acetamiprid
502	tralomethrin	imidacloprid
503	tralomethrin	
504	tralomethrin	nitenpyram nidinotefuran
505	tralomethrin	
506	traiomethrin	chlorfenapyr
		fenpyroximate
507	tralomethrin	tebufenpyrad
508	tralomethrin	fipronil
509	tralomethrin	tebufenozide

510	tralomethrin	methoxyfenozide
511	tralomethrin	halofenozide
512	tralomethrin	triazamate
513	tralomethrin	avermectin
514	tralomethrin	spinosad
		•
515	tralomethrin	acephate
516	tralomethrin	fenamiphos
517	tralomethrin	diazinon
518	tralomethrin	chlorpyrifos
519	tralomethrin	chlorpyrifos-methyl
520	tralomethrin	malathion
521	tralomethrin	carbaryl
522	tralomethrin	aldicarb
523	tralomethrin	carbofuran
524	tralomethrin	thiodicarb
525	tralomethrin	oxamyl
020	u alomeu iiii	Oxamyi
526	cycloprothrin	acetamiprid
527	cycloprothrin	imidacloprid
528	cycloprothrin	nitenpyram
529	cycloprothrin	nidinotefuran
530	cycloprothrin	
531	• •	chlorfenapyr
	cycloprothrin	fenpyroximate
532	cycloprothrin	tebufenpyrad
533	cycloprothrin	fipronil
534	cycloprothrin	tebufenozide
535	cycloprothrin	methoxyfenozide
536	cycloprothrin	halofenozide
537	cycloprothrin	triazamate
538	cycloprothrin	avermectin
539	cycloprothrin	spinosad
540	cycloprothrin	acephate
541	cycloprothrin	fenamiphos
542	cycloprothrin	diazinon
543	cycloprothrin	chlorpyrifos
544	cycloprothrin	chlorpyrifos-methyl
545	cycloprothrin	malathion
546	cycloprothrin	carbaryl
547	cycloprothrin	aldicarb
548	cycloprothrin	carbofuran
549	cycloprothrin	thiodicarb
550	cycloprothrin	oxamyl
000	Cyclopioninii	Oxamy
551	kadethrin	acetamiprid
552	kadethrin	imidacloprid
553	kadethrin	nitenpyram
554	kadethrin	nidinotefuran
555	kadethiii	chlorfenapyr
556	kadethrin	fenpyroximate
550	naueumm	ichpyroximale

557	kadethrin	tebufenpyrad
558	kadethrin	fipronil
559	kadethrin	tebufenozide
560	kadethrin	methoxyfenozide
561	kadethrin	halofenozide
562	kadethrin	triazamate
563	kadethrin	avermectin
564	kadethrin	spinosad
565	kadethrin	· acephate
566	kadethrin	fenamiphos
567	kadethrin	diazinon
568	kadethrin	chlorpyrifos
569	kadethrin	chlorpyrifos-methyl
570	kadethrin	malathion
571	kadethrin	carbaryl
572	kadethrin	aldicarb
573	kadethrin	carbofuran
574	kadethrin	thiodicarb
575	kadethrin	oxamyl
373	Raucumii	Oxamyi
576	resmethrin	acetamiprid
577	resmethrin	imidacloprid
578	resmethrin	nitenpyram
579	resmethrin	nidinotefuran
580	resmethrin	chlorfenapyr
581	resmethrin	fenpyroximate
582	resmethrin	tebufenpyrad
583	resmethrin	fipronil
584	resmethrin	tebufenozide
585	resmethrin	methoxyfenozide
586	resmethrin	halofenozide
587	resmethrin	triazamate
588	resmethrin	avermectin
589	resmethrin	spinosad
590	resmethrin	acephate
591	resmethrin	fenamiphos
592	resmethrin	diazinon
593	resmethrin	chlorpyrifos
594	resmethrin	chlorpyrifos-methyl
595	resmethrin	malathion
596	resmethrin	carbaryl
597	resmethrin	aldicarb
598	resmethrin	carbofuran
599	resmethrin	thiodicarb
600	resmethrin	oxamyl
	· = 2	Onani,
601	bioresmethrin	acetamiprid
602	bioresmethrin	imidacloprid
603	bioresmethrin	nitenpyram

WO 02/28186 PCT/US01/42444 29

bioresmethrin	nidinotefuran
	chlorfenapyr
	fenpyroximate
	tebufenpyrad
	fipronil
	tebufenozide
	methoxyfenozide
	halofenozide
	triazamate
	avermectin
	spinosad -
	acephate
	fenamiphos
	diazinon
	chlorpyrifos
	chlorpyrifos-methyl
	malathion
bioresmethrin	carbaryl
bioresmethrin	aldicarb
bioresmethrin	carbofuran
bioresmethrin	thiodicarb
bioresmethrin	oxamyl
tetramethrin	acetamiprid
tetramethrin	imidacloprid
tetramethrin	nitenpyram
tetramethrin	nidinotefuran
tetramethrin	chlorfenapyr
tetramethrin	fenpyroximate
tetramethrin	tebufenpyrad
tetramethrin	fipronil
tetramethrin	tebufenozide
tetramethrin	methoxyfenozide
tetramethrin	halofenozide
tetramethrin	triazamate
tetramethrin	avermectin
	spinosad
	acephate
	fenamiphos
	diazinon
	chlorpyrifos
	chlorpyrifos-methyl
	malathion
	carbaryl
	aldicarb
	carbofuran
	thiodicarb
tetrametinin	oxamyl
	bioresmethrin bioresmethrin tetramethrin

651	phenothrin	acetamiprid
652	phenothrin	imidacloprid
653	phenothrin	nitenpyram
654	phenothrin	nidinotefuran
655	phenothrin	chlorfenapyr
656	, phenothrin	fenpyroximate
657	phenothrin	tebufenpyrad
658	phenothrin	fipronil
659	phenothrin	tebufenozide
660	phenothrin	methoxyfenozide
661	phenothrin	halofenozide
662	phenothrin	triazamate
663	phenothrin	avermectin
664	phenothrin	·
665	phenothrin	spinosad
666	•	acephate
	phenothrin	fenamiphos
667	phenothrin	diazinon
668	phenothrin	chlorpyrifos
669	phenothrin	chlorpyrifos-methyl
670	phenothrin	malathion
671	phenothrin	carbaryl
672	phenothrin	aldicarb
673	phenothrin	carbofuran
674	phenothrin	thiodicarb
675	phenothrin	oxamyl
070		
676	empenthrin	acetamiprid
677	empenthrin	imidacloprid 
678	empenthrin	nitenpyram
679	empenthrin	nidinotefuran
680	empenthrin	chlorfenapyr
681	empenthrin	fenpyroximate
682	empenthrin	tebufenpyrad
683	empenthrin	fipronil
684	empenthrin	tebufenozide
685	empenthrin	methoxyfenozide
686	empenthrin	halofenozide
687	empenthrin	triazamate
688	empenthrin	avermectin
689	empenthrin	spinosad
690	empenthrin	acephate
691	empenthrin	fenamiphos
692	empenthrin	diazinon
693	empenthrin	chlorpyrifos
694	empenthrin	chlorpyrifos-methyl
695	empenthrin	malathion
696	empenthrin	carbaryl
697	empenthrin	aldicarb
698	empenthrin	carbofuran
	Opontinii	Jaisolalail

699	empenthrin	thiodicarb
700	empenthrin	oxamyl
		•
701	cyphenothrin	acetamiprid
702	cyphenothrin	imidacloprid
703	cyphenothrin	nitenpyram
704	cyphenothrin	nidinotefuran
705	cyphenothrin	chlorfenapyr
706	cyphenothrin	fenpyroximate
707	cyphenothrin	tebufenpyrad
708	cyphenothrin	fipronil
709	cyphenothrin	tebufenozide
710	cyphenothrin	methoxyfenozide
711	cyphenothrin	halofenozide
712	cyphenothrin	triazamate
713	cyphenothrin	avermectin
714	cyphenothrin	spinosad
715	cyphenothrin	acephate
716	cyphenothrin	fenamiphos
717	cyphenothrin	diazinon
717	cyphenothrin	chlorpyrifos
710 719	cyphenothrin	chlorpyrifos-methyl
71 <del>9</del> 720	cyphenothrin	malathion
720 721	* *	
722	cyphenothrin	carbaryl aldicarb
723	cyphenothrin	carbofuran
723 724	cyphenothrin	thiodicarb
	cyphenothrin	
725	cyphenothrin	oxamyl
726	prallethrin	acetamiprid
727	prallethrin	imidacloprid
728	prallethrin	nitenpyram
729	prallethrin	nidinotefuran
730	prallethrin	chlorfenapyr
731	prallethrin	fenpyroximate
732	prallethrin	tebufenpyrad
733	prallethrin	fipronil
734	prallethrin	tebufenozide
735	prallethrin	methoxyfenozide
736	prallethrin	halofenozide
737	prallethrin	triazamate
738	prallethrin	avermectin
739	prallethrin	spinosad
740	prallethrin	acephate
741	prallethrin	fenamiphos
742	prallethrin	diazinon
743	prallethrin	chlorpyrifos
744	prallethrin	chlorpyrifos-methyl
745	prallethrin	malathion
7-70	pranedim	madinon

746	prallethrin	carbaryl
747	prallethrin	aldicarb
748	prallethrin	carbofuran
749	prallethrin	thiodicarb
750	prallethrin	oxamyl
. 00	promoti in in	Oxamy!
751	imiprothrin	acetamiprid
752	imiprothrin	imidacloprid
753	imiprothrin	nitenpyram
754	imiprothrin	nidinotefuran
755	imiprothrin	chlorfenapyr
756	imiprothrin	fenpyroximate
757	imiprothrin	tebufenpyrad
757 758	imiprothrin	
	•	fipronil tebufenozide
759 760	imiprothrin	
760	imiprothrin	methoxyfenozide
761	imiprothrin	halofenozide
762	imiprothrin	triazamate
763	imiprothrin	avermectin
764	imiprothrin	spinosad
765	imiprothrin	acephate
766	imiprothrin	fenamiphos
767	imiprothrin	diazinon
768	imiprothrin	chlorpyrifos
769	imiprothrin	chlorpyrifos-methyl
770	imiprothrin	malathion
771	imiprothrin	carbaryl
772	imiprothrin	aldicarb
773	imiprothrin	carbofuran
774	imiprothrin	thiodicarb
775	imiprothrin	oxamyl
776	allethrin	acetamiprid
777	allethrin	imidacloprid
778	allethrin	nitenpyram
779	allethrin	nidinotefuran
780	allethrin	chlorfenapyr
781	allethrin	fenpyroximate
782	allethrin	tebufenpyrad
783	allethrin	fipronil
784	allethrin	tebufenozide
785	allethrin	methoxyfenozide
786	allethrin	halofenozide
<b>7</b> 87	allethrin	triazamate
788	allethrin	avermectin
789	allethrin	spinosad
790	allethrin	acephate
791	allethrin	fenamiphos
792	allethrin	diazinon

PCT/US01/42444 WO 02/28186

793 794 795 796 797 798 799 800	allethrin allethrin allethrin allethrin allethrin allethrin allethrin	chlorpyrifos chlorpyrifos-methyl malathion carbaryl aldicarb carbofuran thiodicarb oxamyl
000	anounn	Oxamyi
801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821	bioallethrin	acetamiprid imidacloprid nitenpyram nidinotefuran chlorfenapyr fenpyroximate tebufenpyrad fipronil tebufenozide methoxyfenozide halofenozide triazamate avermectin spinosad acephate fenamiphos diazinon chlorpyrifos chlorpyrifos-methyl malathion carbaryl
822 823 824 825	bioallethrin bioallethrin bioallethrin bioallethrin	aldicarb carbofuran thiodicarb oxamyl

#### Note:

a. The composition comprises the two insecticides that appear on the same line as the number of the composition.

5

10

When the other insecticide is an oxadiazine derivative, it has been found that it is preferred that the at least one pyrethroid be selected from the group consisting of taufluvalinate, flumethrin, transcyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

10

15

20

25

30

In another embodiment, the subject method comprises treating a seed prior to sowing with a composition comprising a nitroguanidine and at least one other insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.

It has also been found that a transgenic seed can be protected against multiple pests when the seed has at least one heterologous gene encoding for the expression of a protein that is active against a first pest and, in addition, having adhered thereto a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. It is preferred that the composition containing the synergistic combination of insecticides is present in an amount effective to provide protection to the shoots and foliage of the plant against damage by at least one second pest.

encoding for the expression of a protein that is active against a first pest, the seed can be treated with a combination of insecticides, which combination has activity against at least one second pest. The present method can be used when the first pest and the second pest are the same, for the purpose, for example, to obtain effective control of a particularly resistant or highly damaging pest. But in a separate embodiment, the transgenic trait protects the seed and/or plant from a first pest and the composition of the combination of insecticides is selected to control a second pest that is different from the first pest. This method is particularly advantageous when an expressed transgenic gene provides a gene product that can protect a transgenic plant from one pest, but has no activity against a second, different pest.

In this case, a combination of insecticides of the present invention can

When the transgenic seed has at least one heterologous gene

10

15

20

25

30

be selected that has activity against the second pest, thus providing the seed and plant with protection from both pests. By way of explanation, when a "first" pest and a "second" pest are referred to herein, it should be understood that each of the terms can include only one pest, or can include two or more pests.

It is contemplated that the present method can be used to protect the seeds, roots and/or the above-ground parts of field, forage, plantation, glasshouse, orchard or vineyard crops, ornamentals, plantation or forest trees. The seeds that are useful in the present invention can be the seeds of any species of plant. However, they are preferably the seeds of plant species that are agronomically important. In particular, the seeds can be of corn, peanut, canola/rapeseed, soybean, curcubits, crucifers, cotton, beets, rice, sorghum, sugar beet, wheat, barley, rye, sunflower, tomato, sugarcane, tobacco, oats, as well as other vegetable and leaf crops. It is preferred that the seed be corn, soybeans, or cotton seed; and more preferred that the seeds be corn seeds.

In one embodiment of the invention, as mentioned above, the seed is a transgenic seed from which a transgenic plant can grow. The transgenic seed of the present invention is engineered to express a desirable characteristic and, in particular, to have at least one heterologous gene encoding for the expression of a protein that is pesticidally active and, in particular, has insecticidal activity. The heterologous gene in the transgenic seeds of the present invention can be derived from a microorganism such as Bacillus, Rhizobium, Pseudomonas, Serratia, Trichoderma, Clavibacter, Glomus, Gliocladium and mycorrhizal fungi. In particular, it is believed that the present method would be especially beneficial when the heterologous gene is one that is derived from a Bacillus sp. microorganism and the protein is active against corn rootworm. It is also believed that the present method would be especially beneficial when the heterologous gene is one that is derived from a Bacillus sp. microorganism and the protein is active against European corn borer. A preferred Bacillus sp.

microorganism is *Bacillus thuringiensis*. It is particularly preferred when the heterologous gene encodes a modified Cry3Bb delta-endotoxin derived from *Bacillus thuringiensis*, as disclosed, for example, in U.S. Patent No. 6,063,597.

5

The target pest for the present invention is an adult or larvae of any insect or other pest that feeds on the seed, roots and/or shoots and foliage of the plant that is to be protected by the subject method. Such pests include but are not limited to: from the order Lepidoptera, for example,

10

15

20

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argillaceae, Amylois spp., Anticarsia gemmatalis, Archips spp, Argyrotaenia spp., Autographa spp., Busseola fusca, Cadra cautella, Carposina nipponensis, Chilo spp., Choristoneura spp., Clysia ambiguella, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Crocidolomia binotalis, Cryptophlebia leucotreta. Cydia spp., Diatraea spp., Diparopsis castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia Nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiella, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp.,

25

30

Agriotes spp., Anthonomus spp., Atomaria linearis,
Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes
spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa
decemlineata, Lissorhoptrus spp., Melolontha spp., Orycaephilus spp.,
Otiorhynchus spp., Phlyctinus spp., Popillia spp., Psylliodes spp.,

Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta

spp.; from the order Coleoptera, for example,

20

25

30

Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.; from the order Orthoptera, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta ssp., and Schistocerca spp.; from the order Isoptera, for example,

Reticulitemes ssp;

from the order Psocoptera, for example,

Liposcelis spp.;

from the order Anoplura, for example,

Haematopinus spp., Linognathus spp., Pediculus spp.,

Pemphigus spp. and Phylloxera spp.;

from the order Mallophaga, for example,

Damalinea spp. and Trichodectes spp.;

from the order Thysanoptera, for example,

Franklinella spp., Hercinothrips spp., Taeniothrips spp., *Thrips* palmi, *Thrips tabaci and Scirtothrips aurantii*; from the order Heteroptera, for example,

Cimex spp., *Distantiella theobroma*, Dysdercus spp., Euchistus spp., Eurygaster spp., Leptocorisa spp., Nezara spp., Piesma spp., Rhodnius spp., *Sahlbergella singularis*, Scotinophara spp. and Triatoma spp.;

from the order Homoptera, for example,

Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Bemisia tabaci, Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Coccus hesperidum, Empoasca spp., Eriosoma larigerum, Erythroneura spp., Gascardia spp., Laodelphax spp., Lacanium corni, Lepidosaphes spp., Macrosiphus spp., Myzus spp., Nehotettix spp., Nilaparvata spp., Paratoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp., Pseudococcus spp., Psylla ssp., Pulvinaria aethiopica,

Quadraspidiotus spp., Rhopalosiphum spp., Saissetia spp.,

Scaphoideus spp., Schizaphis spp., Sitobion spp., *Trialeurodes* vaporariorum, *Trioza erytreae* and *Unaspis citri*; from the order Hymenoptera, for example,

Acromyrmex, Atta spp., Cephus spp., Diprion spp., Diprionidae, *Gilpinia polytoma*, Hoplocampa spp., Lasius sppp., *Monomorium pharaonis*, Neodiprion spp, Solenopsis spp. and Vespa ssp.; from the order Diptera, for example,

Aedes spp., Antherigona soccata, Bibio hortulanus, Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp., Drosophila melanogaster, Fannia spp., Gastrophilus spp., Glossina spp., Hypoderma spp., Hyppobosca spp., Liriomysa spp., Lucilia spp., Melanagromyza spp., Musca ssp., Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami, Phorbia spp., Rhagoletis pomonella, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.,

from the order Siphonaptera, for example,

Ceratophyllus spp. und *Xenopsylla cheopis* and from the order Thysanura, for example,

Lepisma saccharina.

20

25

30

15

5

10

In each embodiment of the invention, it is preferred that a combination of two or more insecticides is applied to a seed in an effective amount; that is, an amount sufficient to provide protection to the seed and/or shoots and foliage of the plant that grows from the seed. As used herein, "protection" is achieved if the percent of feeding damage to the seed and/or the shoots and foliage at 10 days after infestation (DAI) with the pest is reduced for treated seeds or plants grown from treated seeds as compared to untreated seeds or plants grown from untreated seeds. In a preferred embodiment, an unexpected advantage of the compositions of the present invention is that the component insecticides of the composition operate synergistically. As used here, when it is said that a combination demonstrates "synergy", what is meant is that the degree of protection that is provided to a seed and/or the shoots and foliage of a plant that

10

15

20

25

30

grows from a seed, by treatment of the seed by the present method (using a combination of insecticides), is superior to the degree of protection that would be expected on the basis of the protection provided by each of the components of the composition applied separately.

PCT/US01/42444

Methods for the calculation of whether a particular insecticide combination provides synergy are described in detail in the Examples. Briefly stated, however, whether a combination of insecticides provided synergy in protection against cutworm damage can be calculated as described by Colby, Robert. S., in *Weeds*, *15*(*1*):20 - 22 (1967). The threshold value (stated as % of control) for synergy of a combination was calculated as = (% of control for treatment A)\*(% of control for treatment B)/100(n-1); where n = number of active ingredients in the combination. A measured % of control value that is less than the calculated threshold value indicates synergy of the combination.

When the "degree of protection" is mentioned herein, it is meant to include the amount of damage caused by the target insect to seeds that have been treated with a given amount of insecticide (and the plants that sprout therefrom) relative to the amount of damage caused to untreated seeds and plants. But "degree of protection" can also refer to the number of different types of target pests that are affected by the treatment and the length of the period of protection. In other words, a synergistic degree of protection can include unexpectedly effective protection at reduced levels of active ingredient, as well as protection against an unexpectedly wide variety of pests, or protection for an unexpectedly long (or otherwise particularly effective) period of time.

The amount of the insecticidal composition of the present invention that will provide protection to plant shoots and foliage will vary depending on the particular pesticide combination, the concentration of active ingredients in the composition, the nature of the formulation in which it is applied, the seed type, and the target pest(s). As used herein, an amount of the composition effective to provide

protection to the seed and/or shoots and foliage of the plant against damage by the pest is the lowest amount of such pesticide that will provide such protection. Assuming that the composition is comprised of 100% active ingredients, then, in general, the amount of the subject composition used will range from about 0.005% to 25% of the weight of the seed, and more preferably, from about 0.01% to about 10%. A yet more preferred range is 0.01% to 1% of the active ingredients relative to the weight of the seed, and an even more preferred range is 0.05% to 0.5%.

10

5

The subject compositions are each composed of at least two insecticidal compounds, such as the combinations described in Table 1, and in the surrounding text. When two components are used, the relative amounts of the two insecticides can range from 1:1000 to 1000:1, by weight. It is preferred, however, that the weight ratio of the two insecticides range from 1:100 to 100:1, more preferred is a ratio of 1:10 to 10:1, and yet more preferred is a ratio of 1:3 to 3:1.

15

20

25

30

In the method of the present invention, the combination of pesticides is applied to a seed. Although it is believed that the present method can be applied to a seed in any physiological state, it is preferred that the seed be in a sufficiently durable state that it incurs no damage during the treatment process. Typically, the seed would be a seed that had been harvested from the field; removed from the plant; and separated from any cob, stalk, outer husk, and surrounding pulp or other non-seed plant material. The seed would preferably also be biologically stable to the extent that the treatment would cause no biological damage to the seed. In one embodiment, for example, the treatment can be applied to seed corn that has been harvested, cleaned and dried to a moisture content below about 15% by weight. In an alternative embodiment, the seed can be one that has been dried and then primed with water and/or another material and then re-dried before or during the treatment with the pesticide. Within the limitations just described, it is believed that the treatment can be applied to the

seed at any time between harvest of the seed and sowing of the seed.

As used herein, the term "unsown seed" is meant to include seed at any period between the harvest of the seed and the sowing of the seed in the ground for the purpose of germination and growth of the plant.

When it is said that unsown seed is "treated" with the composition, such treatment is not meant to include those practices in which the pesticide is applied to the soil, rather than to the seed. For example, such treatments as the application of the pesticide in bands, "T"-bands, or in-furrow, at the same time as the seed is sowed are not considered to be included in the present invention.

10

15

20

5

The composition comprising a combination of pesticides can be applied "neat", that is, without any diluting or additional components present. However, the composition is typically applied to the seeds in the form of a pesticide formulation. This formulation may contain one or more other desirable components including but not limited to liquid diluents, binders to serve as a matrix for the pesticide, fillers for protecting the seeds during stress conditions, and plasticizers to improve flexibility; adhesion and/or spreadability of the coating. In addition, for oily pesticide formulations containing little or no filler, it may be desirable to add to the formulation drying agents such as calcium carbonate, kaolin or bentonite clay, perlite, diatomaceous earth or any other adsorbent material. Use of such components in seed treatments is known in the art. See, e.g., U.S. Patent No. 5,876,739. The skilled artisan can readily select desirable components to use in the pesticide formulation depending on the seed type to be treated and the particular pesticide that is selected. In addition, readily available commercial formulations of known pesticides may be used, as demonstrated in the examples below.

25

30

The seeds may also be treated with one or more of the following ingredients: other pesticides, including compounds which act only below the ground; fungicides, such as captan, thiram, metalxyl, fludioxonil, oxadixyl, and isomers of each of those materials, and the like; herbicides, including compounds selected from carbamates, thiocarbamates, acetamides, triazines, dinitroanilines, glycerol ethers,

pyridazinones, uracils, phenoxys, ureas, and benzoic acids; herbicidal safeners such as benzoxazine, benzhydryl derivatives, N,N-diallyl dichloroacetamide, various dihaloacyl, oxazolidinyl and thiazolidinyl compounds, ethanone, naphthalic anhydride compounds, and oxime derivatives; fertilizers; and biocontrol agents such as naturally-occurring or recombinant bacteria and fungi from the genera *Rhizobium*, *Bacillus*, *Pseudomonas*, *Serratia*, *Trichoderma*, *Glomus*, *Gliocladium* and mycorrhizal fungi. These ingredients may be added as a separate layer on the seed or alternatively may be added as part of the pesticide composition.

Preferably, the amount of the novel composition or other ingredients used in the seed treatment should not inhibit generation of the seed, or cause phytotoxic damage to the seed.

The composition of the present invention can be in the form of a suspension; emulsion; slurry of particles in an aqueous medium (e.g., water); wettable powder; wettable granules (dry flowable); and dry granules. If formulated as a suspension or slurry, the concentration of the active ingredient in the formulation is preferably about 0.5% to about 99% by weight (w/w), preferably 5-40%.

20

25

30

5

10

15

As mentioned above, other conventional inactive or inert ingredients can be incorporated into the formulation. Such inert ingredients include but are not limited to: conventional sticking agents, dispersing agents such as methylcellulose (Methocel A15LV or Methocel A15C, for example, serve as combined dispersant/sticking agents for use in seed treatments), polyvinyl alcohol (e.g., Elvanol 51-05), lecithin (e.g., Yelkinol P), polymeric dispersants (e.g., polyvinylpyrrolidone/vinyl acetate PVP/VA S-630), thickeners (e.g., clay thickeners such as Van Gel B to improve viscosity and reduce settling of particle suspensions), emulsion stabilizers, surfactants, antifreeze compounds (e.g., urea), dyes, colorants, and the like. Further inert ingredients useful in the present invention can be found in McCutcheon's, vol. 1, "Emulsifiers and Detergents," MC Publishing Company, Glen Rock, New Jersey, U.S.A., 1996. Additional inert

10

15

20

25

30

ingredients useful in the present invention can be found in McCutcheon's, vol. 2, "Functional Materials," MC Publishing Company, Glen Rock, New Jersey, U.S.A., 1996.

The pesticides, compositions of pesticide combinations, and formulations of the present invention can be applied to seeds by any standard seed treatment methodology, including but not limited to mixing in a container (e.g., a bottle or bag), mechanical application, tumbling, spraying, and immersion. Any conventional active or inert material can be used for contacting seeds with pesticides according to the present invention, such as conventional film-coating materials including but not limited to water-based film coating materials such as Sepiret (Seppic, Inc., Fairfield, NJ) and Opacoat (Berwind Pharm. Services, Westpoint, PA).

The subject combination of pesticides can be applied to a seed as a component of a seed coating. Seed coating methods and compositions that are known in the art are useful when they are modified by the addition of one of the embodiments of the combination of pesticides of the present invention. Such coating methods and apparatus for their application are disclosed in, for example, U.S. Patent Nos. 5,918,413, 5,891,246, 5,554,445, 5,389,399, 5,107,787, 5,080,925, 4,759,945 and 4,465,017. Seed coating compositions are disclosed, for example, in U.S. Patent Nos. 5,939,356, 5,882,713, 5,876,739, 5,849,320, 5,834,447, 5,791,084, 5,661,103, 5,622,003, 5,580,544, 5,328,942, 5,300,127, 4,735,015, 4,634,587, 4,383,391, 4,372,080, 4,339,456, 4,272,417 and 4,245,432, among others.

Useful seed coatings contain one or more binders and at least one of the subject combinations of pesticides.

Binders that are useful in the present invention preferably comprise an adhesive polymer that may be natural or synthetic and is without phytotoxic effect on the seed to be coated. The binder may be selected from polyvinyl acetates; polyvinyl acetate copolymers; polyvinyl alcohols; polyvinyl alcohol copolymers; celluloses, including ethylcelluloses, methylcelluloses, hydroxymethylcelluloses,

10

15

20

25

30

hydroxypropylcelluloses and carboxymethylcellulose; polyvinylpyrolidones; polysaccharides, including starch, modified starch, dextrins, maltodextrins, alginate and chitosans; fats; oils; proteins, including gelatin and zeins; gum arabics; shellacs; vinylidene chloride and vinylidene chloride copolymers; calcium lignosulfonates; acrylic copolymers; polyvinylacrylates; polyethylene oxide; acrylamide polymers and copolymers; polyhydroxyethyl acrylate, methylacrylamide monomers; and polychloroprene.

It is preferred that the binder be selected so that it can serve as a matrix for the subject combination of pesticides. While the binders disclosed above may all be useful as a matrix, the specific binder will depend upon the properties of the combination of pesticides. The term "matrix", as used herein, means a continuous solid phase of one or more binder compounds throughout which is distributed as a discontinuous phase one or more of the subject combinations of pesticides. Optionally, a filler and/or other components can also be present in the matrix. The term matrix is to be understood to include what may be viewed as a matrix system, a reservoir system or a microencapsulated system. In general, a matrix system consists of a combination of pesticides of the present invention and filler uniformly dispersed within a polymer, while a reservoir system consists of a separate phase comprising the subject combination of pesticides, that is physically dispersed within a surrounding, rate-limiting, polymeric phase. Microencapsulation includes the coating of small particles or droplets of liquid, but also to dispersions in a solid matrix.

The amount of binder in the coating can vary, but will be in the range of about 0.01 to about 25% of the weight of the seed, more preferably from about 0.05 to about 15%, and even more preferably from about 0.1% to about 10%.

As mentioned above, the matrix can optionally include a filler. The filler can be an absorbent or an inert filler, such as are known in the art, and may include woodflours, clays, activated carbon, sugars, diatomaceous earth, cereal flours, fine-grain inorganic solids, calcium

10

15

20

25

30

carbonate, and the like. Clays and inorganic solids which may be used include calcium bentonite, kaolin, china clay, talc, perlite, mica, vermiculite, silicas, quartz powder, montmorillonite and mixtures thereof. Sugars which may be useful include dextrin and maltodextrin. Cereal flours include wheat flour, oat flour and barley flour.

The filler is selected so that it will provide a proper microclimate for the seed, for example the filler is used to increase the loading rate of the active ingredients and to adjust the control-release of the active ingredients. The filler can aid in the production or process of coating the seed. The amount of filler can vary, but generally the weight of the filler components will be in the range of about 0.05 to about 75% of the seed weight, more preferably about 0.1 to about 50%, and even more preferably about 0.5% to 15%.

The pesticides that are useful in the coating are those combinations of pesticides that are described herein. The amount of pesticide that is included in the coating will vary depending upon the type of seed and the type of active ingredients, but the coating will contain an amount of the combination of pesticides that is pesticidally effective. When insects are the target pest, that amount will be an amount of the combination of insecticides that is insecticidally effective. As used herein, an insecticidally effective amount means that amount of insecticide that will kill insect pests in the larvae or pupal state of growth, or will consistently reduce or retard the amount of damage produced by insect pests. In general, the amount of pesticide in the coating will range from about 0.005 to about 50% of the weight of the seed. A more preferred range for the pesticide is from about 0.01 to about 40%; more preferred is from about 0.05 to about 20%.

The exact amount of the combination of pesticides that is included in the coating is easily determined by one of skill in the art and will vary depending upon the size of the seed to be coated. The pesticides of the coating must not inhibit germination of the seed and should be efficacious in protecting the seed and/or the plant during that time in the target insect's life cycle in which it causes injury to the seed

or plant. In general, the coating will be efficacious for approximately 0 to 120 days after sowing.

The coating is particularly effective in accommodating high pesticidal loads, as can be required to treat typically refractory pests, such as corn root worm, while at the same time preventing unacceptable phytotoxicity due to the increased pesticidal load.

Optionally, a plasticizer can be used in the coating formulation. Plasticizers are typically used to make the film that is formed by the coating layer more flexible, to improve adhesion and spreadability, and to improve the speed of processing. Improved film flexibility is important to minimize chipping, breakage or flaking during storage, handling or sowing processes. Many plasticizers may be used, however, useful plasticizers include polyethylene glycol, glycerol, butylbenzylphthalate, glycol benzoates and related compounds. The range of plasticizer in the coating layer will be in the range of from bout 0.1 to about 20% by weight.

When the combination of pesticides used in the coating is an oily type formulation and little or no filler is present, it may be useful to hasten the drying process by drying the formulation. This optional step may be accomplished by means will known in the art and can include the addition of calcium carbonate, kaolin or bentonite clay, perlite, diatomaceous earth, or any absorbent material that is added preferably concurrently with the pesticidal coating layer to absorb the oil or excess moisture. The amount of calcium carbonate or related compounds necessary to effectively provide a dry coating will be in the range of about 0.5 to about 10% of the weight of the seed.

The coatings formed with the combination of pesticides are capable of effecting a slow rate of release of the pesticide by diffusion or movement through the matrix to the surrounding medium.

The coating can be applied to almost any crop seed that is described herein, including cereals, vegetables, ornamentals and fruits.

In addition to the coating layer, the seed may be treated with one or more of the following ingredients: other pesticides including

10

5

15

20

25

fungicides and herbicides; herbicidal safeners; fertilizers and/or biocontrol agents. These ingredients may be added as a separate layer or alternatively may be added in the pesticidal coating layer.

The pesticide formulation may be applied to the seeds using conventional coating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed treaters, and drum coaters. Other methods, such as spouted beds may also be useful. The seeds may be presized before coating. After coating, the seeds are typically dried and then transferred to a sizing machine for sizing. Such procedures are known in the art.

The pesticide-treated seeds may also be enveloped with a film overcoating to protect the pesticide coating. Such overcoatings are known in the art and may be applied using conventional fluidized bed and drum film coating techniques.

15

20

25

10

5

In another embodiment of the present invention, a pesticide can be introduced onto or into a seed by use of solid matrix priming. For example, a quantity of the pesticide can be mixed with a solid matrix material and then the seed can be placed into contact with the solid matrix material for a period to allow the pesticide to be introduced to the seed. The seed can then optionally be separated from the solid matrix material and stored or used, or the mixture of solid matrix material plus seed can be stored or planted directly. Solid matrix materials which are useful in the present invention include polyacrylamide, starch, clay, silica, alumina, soil, sand, polyurea, polyacrylate, or any other material capable of absorbing or adsorbing the pesticide for a time and releasing that pesticide into or onto the seed. It is useful to make sure that the pesticide and the solid matrix material are compatible with each other. For example, the solid matrix material should be chosen so that it can release the pesticide at a reasonable rate, for example over a period of minutes, hours, or days.

30

The present invention further embodies imbibition as another method of treating seed with the pesticide. For example, plant seed can be combined for a period of time with a solution comprising from

about 1% by weight to about 75% by weight of the pesticide in a solvent such as water. Preferably the concentration of the solution is from about 5% by weight to about 50% by weight, more preferably from about 10% by weight to about 25% by weight. During the period that the seed is combined with the solution, the seed takes up (imbibes) a portion of the pesticide. Optionally, the mixture of plant seed and solution can be agitated, for example by shaking, rolling, tumbling, or other means. After imbibition, the seed can be separated from the solution and optionally dried, for example by patting or air drying.

10

5

In yet another embodiment, a powdered pesticide can be mixed directly with seed. Optionally, a sticking agent can be used to adhere the powder to the seed surface. For example, a quantity of seed can be mixed with a sticking agent and optionally agitated to encourage uniform coating of the seed with the sticking agent. The seed coated with the sticking agent can then be mixed with the powdered pesticide. The mixture can be agitated, for example by tumbling, to encourage contact of the sticking agent with the powdered pesticide, thereby causing the powdered pesticide to stick to the seed.

20

15

The present invention also provides a seed that has been treated by the method described above.

propagation of plants in the same manner as conventional treated seed. The treated seeds can be stored, handled, sowed and tilled in the same manner as any other pesticide treated seed. Appropriate safety measures should be taken to limit contact of the treated seed with humans, food or feed materials, water and birds and wild or

The treated seeds of the present invention can be used for the

30

25

domestic animals.

Preferred embodiments of the invention are described in the following examples. Other embodiments within the scope of the claims herein will be apparent to one skilled in the art from consideration of the specification or practice of the invention as disclosed herein. It is intended that the specification, together with the examples, be

10

15

20

25

30

considered exemplary only, with the scope and spirit of the invention being indicated by the claims which follow the examples.

### REFERENCE EXAMPLE 1

This example compares the efficacy of seed treatment with lambda-cyhalothrin (CAS# 91465-08-6) to soil granular treatments with tefluthrin (CAS # 79538-32-2) against feeding damage by black cutworm larvae on shoots and foliage.

A lambda-cyhalothrin seed treatment formulation was prepared by diluting the WARRIOR® T insecticide (Zeneca Ag Products, Wilmington, DE), which contains 11.4% lambda-cyhalothrin as the active ingredient, into water as a carrier. This formulation was applied for one minute at room temperature to twenty-five grams of Pioneer corn seed (Cultivar PN3394) in a rotostatic seed treater at a rate of 125 g, 250 g or 500 g active ingredient (Al) to 100 kg seed. The treated seeds were allowed to sit uncapped for four to twenty-four hours before planting.

Treated and untreated seeds (Pioneer hybrid PN3394) were planted in a soil mix consisting of Dupo silt loam, 30% Perlite, 20% coarse sand (WB-10 grade) in six groups of tubs (20 in. L X 15 in. W X 8 in. D). Twelve seeds were planted per tub and three tubs were planted for each treatment regimen. Soil applications of FORCE® 3GR, which contains 3% tefluthrin granule as the active ingredient, were used for two sets of tubs containing untreated seeds. The FORCE 3GR was applied either in-furrow or incorporated into a 5 inch band on the soil surface at the time of planting. The tubs were overhead irrigated until the plants were infested with black cutworm larvae.

The rate of application for the FORCE 3GR was reported in units of grams of the active ingredient per hectare (g/ha), while the rate of application of the WARRIOR T to the seeds was reported in units of grams of the active ingredient per 100 kilograms of the seeds (g/100 kg). Although the conversion of one of these units to the other will vary somewhat according to the type of seed that is being used, the size

VO 02/28186 PCT/US01/42444

and weight of the seed, and the density of planting that is used -- among other things -- an approximate conversion for corn seed can be carried out as follows. Assuming a seed application rate of lambda cyhalothrin of, for example, 125g/100 kg of seed and a planting density of 15 lbs seed/ac, about 14.7 acres can be planted with 100 kg of the seed. This is an effective application rate of about 8.5g of lambda cyhalthrin per acre. At 2.47 ac/ha, the seed treatment level of 125g/100 kg is approximately equivalent to a surface banding treatment at about 21g/ha.

10

5

At twelve days after planting (DAP) but before infestation, the overall health of each plant was rated by looking at emergence, height and appearance. This vigor rating gives an indication of any phytotoxicity from the seed or soil treatment. A rating of 1 indicates extremely low vigor while 10 is the highest vigor rating.

15

20

The corn plants were infested at 12 DAP, which corresponds to late growth stage V1 by placing two black cutworm larvae at 3/4 instar on the soil surface near the base of the plant. Plants were rated 3, 7 and 10 days after infestation (DAI) for the number of cut plants, as well as damage from leaf feeding. The percent stand reduction due to plant cutting was calculated by dividing the number of cut plants into the number of plants present at infestation. The foliar feeding injury was evaluated using a rating scale of 1 = no damage and 10 = complete defoliation. The mean results for the three tubs for each treatment regimen are presented in Table 2 below.

25

Table 2. Efficacy of lambda-cyhalothrin seed-treatment against black cutworm feeding damage on corn.

10

15

Treatment Regimen	Vigor at 12 DAP	% Stand Reduct'n 3 DAI	Plant Defol. 3 DAI	% Stand Reduct'n 7 DAI	Plant Defol. 7 DAI	% Stand Reduct'n 10 DAI	Plant Defol. 10 DAI
None	8.0	72.8	9.0	94.4	9.3	100.0	10.0
λ- cyhalothrin seed 125 g/100 kg	9.0	13.9	4.3	16.7	5.0	19.4	3.3
λ- cyhalothrin seed 250 g/100 kg	8.3	3.0	3.7	3.0	2.7	3.0	1.7
λ- cyhalothrin seed 500 g/100 kg	8.3	0.0	2.0	0.0	2.3	0.0	1.0
Tefluthrin in-furrow 30 g/ha	9.0	33.9	5.0	48.0	6.0	48.0	5.3
Tefluthrin banded 30 g/ha	8.7	0.0	1.7	0.0	1.7	0.0	0.3

These results demonstrate that seed treatment with lambdacyhalothrin prior to planting provides significant protection of corn plants against shoot/foliar feeding damage by black cutworm. For example, at 7 DAI with the lowest rate tested (125 g/kg seed), a significant reduction was observed for both plant cutting (16.7% for seed treatment vs. 94% for untreated control) and foliar feeding injury (5.0 for seed treatment vs. 9.3 rating for untreated control) In addition, tubs planted with seed treated with lambda-cyhalothrin at rates of 250 and 500 g/100 kg seed, showed essentially no stand reduction from plant cutting (3% and 0% for 250 and 500 g, respectively) and only low levels of foliar injury (2.7 and 2.3 rating for 250 and 500 g, respectively). This level of protection was equal to the tefluthrin soil band treatment and superior to tefluthrin in-furrow treatment. When the tubs were evaluated at 10 DAI, no increase in plant cutting and only

slightly higher ratings for foliar feeding injury were observed with lambda-cyhalothrin seed treatments as compared to evaluations at 7 DAI. In contrast, the untreated control tubs exhibited 100% plant cutting and complete defoliation by 10 DAI.

5

10

#### **EXAMPLE 2**

This example illustrates the efficacy of corn seed treatment with a combination of tefluthrin and acephate against plant damage by black cutworm.

Seed treatment formulations were prepared from tefluthrin (available from Wilbur Ellis Co. under the trade name of RAZE® 2.5 FS) and acephate (N-[methoxy(methylthio)phosphinoyl]acetamide; CAS Registry No. 30560-19-1); available from Tomen Agro Inc., San Francisco, CA, or Valent USA Corp., Walnut Creek, CA, under the trade name of ORTHENE®.

15

20

In addition, separate seed treatment formulations were prepared from each of the two insecticides alone and a sample of untreated seed was also prepared. Corn seed was prepared and treated as described in Example 1, except that the treatment levels of the active ingredients on the seeds was as shown in Table 3. Treated and untreated seeds were planted in tubs and cultivated as described in Example 1. The tubs were overhead irrigated until the plants were infested with black cutworm larvae.

The corn plants were infested as 12 DAP, as described in Example 1. Plants were rated at 10 DAI for the number of cut plants. The percent stand reduction due to plant cutting was calculated by dividing the number of cut plants into the number of plants present at infestation. The mean results for each of the seed treatment regimens is presented in Table 3.

30

25

Whether a combination of insecticides provided synergy in protection against cutworm damage was calculated as described by Colby, Robert. S., in *Weeds*, *15(1)*:20 - 22 (1967). The threshold value (stated as % of control) for synergy of a combination was calculated as = (% of control for treatment A)\*(% of control for treatment B)/100(n-1);

10

where n = number of active ingredients in combination. A measured % of control value that is less than the threshold value indicates synergy of the combination. Threshold values for synergy were calculated for each of the combinations of Table 3, and the threshold values for synergy of combinations of the active ingredients at various levels are shown in Table 4.

Table 3: Protection of corn plants against black cutworm damage by seed treatments with tefluthrin, acephate and combinations of the two.

TREATMENT	Tefluthrin (gm/100 kg seed)	Acephate (gm/100 kg seed)	STAND REDUCTION (% at 10 days)	Percent of Control	Synergy
RAZE	100	, , , , , , , , , , , , , , , , , , ,	75	75	
RAZE	200		100	100	
RAZE	300		83	83	
ORTHENE		100	6.3	6.3	
ORTHENE		200	18.4	18.4	
RAZE/ORTH	100	100	9.4	9.4	NO
RAZE/ORTH	100	200	9.4	9.4	YES
RAZE/ORTH	200	100	33	33	NO
RAZE/ORTH	200	200	9.4	9.4	YES
RAZE/ORTH	300	100	13.5	13.5	NO
RAZE/ORTH	300	200	7.1	7.1	YES
UNTREATED CONTROL	0	0	100		,

10

15

Table 4: Matrix of threshold values for synergy of combination (% of control)

	RAZE @ 100	RAZE @ 200	RAZE @ 300
ORTHENE @	4.7	6.3	5.2
100			
ORTHENE @	13.8	18.4	15.3
200			

The results of this test showed that the

pyrethroid/organophosphorous-insecticide combinations of tefluthrin and acephate were synergistic against damage of the plant by black cutworm for all levels of tefluthrin when levels of acephate were 200 gm/100 kg of seed (or about 0.3% by weight of the seed).

In view of the above, it will be seen that the several advantages of the invention are achieved and other advantageous results attained.

As various changes could be made in the above methods and compositions without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

The discussion of references herein is intended merely to summarize the assertions made by their authors and no admission is made that any reference constitutes prior art. Applicants reserve the right to challenge the accuracy and pertinency of the cited references.

#### WHAT IS CLAIMED IS:

1. A method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating an unsown seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.

10

5

2. The method as set forth in claim 1, wherein the at least one other insecticide comprises an oxadizine derivative, and the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.

15

20

25

30

The method as set forth in claim 1 wherein the at least 3. one pyrethrin or synthetic pyrethroid is selected from the group consisting of (s)-cyano(3-phenoxyphenyl)methyl 4-chloro alpha (lmethylethyl)benzeneacetate (fenvalerate); (S)-cyano (3phenoxyphenyl) methyl (S)-4-chloro-alpha-(1-methylethyl) benzeneacetate (esfenvalerate); (3-phenoxyphenyl)-methyl(+)cis-trans-3-(2,2-dichoroethenyl)-2,2-dimethylcyclopropanecarboxylate (permethrin); (±) alpha-cyano-(3-phenoxyphenyl) methyl(+)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylate (cypermethrin); (beta-cypermethrin); (theta cypermethrin); S-cyano (3phenoxyphenyl) methyl (±) cis/trans 3-(2,2-dichloroethenyl) 2,2 dimethylcyclopropane carboxylate (zeta-cypermethrin); (s)-alphacyano-3-phenoxybenzyl (IR,3R)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropanecarboxylate (deltamethrin); alpha-cyano-3-phenoxybenzyl 2,2,3,3,-tetramethyl cyclopropoanecarboxylate (fenpropathrin); (RS)alpha-cyano-3-phenoxybenzyl(R)-2-[2-chloro-4-(trifluoromethyl)anilino]-3-methylbutanoate (tau-fluvalinate); (2,3,5,6-tetrafluoro-4-

methylphenyl)-methyl-(1 alpha, 3 alpha)-(Z)-(±)-3-(2-chloro-3,3,3-

trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (tefluthrin); (±)-cvano (3-phenoxyphenyl) methyl (±)-4-(difluoromethoxy)-alpha-(1methyl ethyl) benzeneacetate (flucythrinate); cyano(4-fluoro-3phenoxyphenyl)methyl 3-[2-chloro-2-(4-chlorophenyl)ethenyl]-2,2-5 dimethylcyclopropanecarboxylate (flumethrin); cyano(4-fluoro-3phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanedarboxylate (cyfluthrin); (beta cyfluthrin); (transfluthrin); (S)-alpha-cyano-3-phenoxybenzyl(Z)-(IR-cis)-2.2-dimethyl-3-[2-(2.2.2trifluoro-trifluoromethyl-ethoxycarbonyl)vinyl]cyclopropane carboxylate 10 (acrinathrin); (IR cis) S and (IS cis) R enantiomer isomer pair of alphacyano-3-phenoxybenzyl-3-(2,2dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (alphacypermethrin); [IR,3S)3(1'RS)(1',2',2',2'tetrabromoethyl)]-2,2-dimethyl cyclopropanecarboxylic acid (s)-alphacyano-3-phenoxybenzyl ester (tralomethrin); cyano-(3-phenoxyphenyl) 15 methyl 2,2-dichloro-1- (4-ethoxyphenyl)cyclopropane carboxylate. (cycloprothrin);  $[1\alpha, 3\alpha(Z)]$ -(±)-cyano-(3-phenoxyphenyl)methyl 3-(2chloro-3,3,3-trifluoro-1-propenyl)-2,2-cimethylcyclopropanecarboxylate (cyhalothrin); [1 alpha (s), 3 alpha(z)]-cyano(3-phenoxyphenyl) methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropane 20 carboxylate (lambda cyhalothrin); (2-methyl [1,1'-biphenyl]-3-yl) methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (bifenthrin); 5-1-benzyl-3-furylmethyl-dcis(1R,3S,E)2,2-dimethyl-3-(2-oxo,-2,2,4,5 tetrahydro thiophenylidenemethyl)cyclopropane carboxylate (kadethrin. 25 RU15525); [5-(phenyl methyl)-3-furanyl]-3-furanyl 2,2-dimethyl-3-(2methyl-1-propenyl) cyclopropane carboxylate (resmethrin); (1R-trans)-[5-(phenylmethyl)-3-furanyl]methyl 2,2-dimethyl-3-(2-methyl-1propenyl)cyclopropanecarboxylate (bioresmethrin); 3.4.5.6-tetra hydrophthalimidomethyl-(IRS)-cis-trans-chrysanthemate (tetramethrin); 3phenoxybenzyl-d,l-cis,trans 2,2-dimethyl-3-(2-methylpropenyl) cyclopropane carboxylate (phenothrin); (empenthrin); (cyphenothrin); (prallethrin); (imiprothrin); (RS)-3-allyl-2-methyl-4-oxcyclopent-2-enyl-

10

15

20

25

30

(1A,3R; 1R,3S)-2,2-dimethyl-3- (2-methylprop-1-enyl) cyclopropane carboxylate (allethrin); (bioallethrin); and (ZXI8901).

- 4. The method as set forth in claim 3, wherein the synthetic pyrethroid is selected from the group consisting of tefluthrin, lambda cyhalothrin, cyfluthrin and bifenthrin.
- 5. The method according to claim 2, wherein the pesticide comprises an oxadiazine derivative.
- 6. The method according to claim 5, wherein the oxadizine derivative comprises an insecticide selected from the group consisting of 5-(2-chloropyrid-5-ylmethyl)-3-methyl-4-nitroiminoperhydro-1,3,5-oxadiazine, 3-methyl-4-nitroimino-5-(1-oxido-3-pyridinomethyl) perhydro-1,3,5-oxadiazine, 5-(2-chloro-1-oxido-5-pyridiniomethyl)-3-methyl-4-nitroiminoperhydro-1,3,5-oxadiazine, and 3-methyl-5-(2-methylpyrid-5-ylmethyl)-4-nitroiminoperhydro-1,3,5-oxadiazine.
- 7. The method as set forth in claim 2, wherein the other insecticide comprises a chloronicotinyl.
- 8. The method as set forth in claim 7, wherein the chloronicotinyl is selected from the group consisting of imidacloprid, acetamiprid and nitenpyram.
- 9. The method as set forth in claim 2, wherein the other insecticide comprises a nitroguanidine.
- 10. The method as set forth in claim 9, wherein the nitroguanidine comprises nidinotefuran.
- 11. The method as set forth in claim 2, wherein the other insecticide comprises a pyrrol.
- 12. The method as set forth in claim 9, wherein the pyrrol comprises chlorfenapyr.
- 13. The method as set forth in claim 2, wherein the other insecticide comprises a pyrazone.
- 14. The method as set forth in claim 13, wherein the pyrazone comprises tebufenpyrad.
- 15. The method as set forth in claim 2, wherein the other insecticide comprises a diacylhydrazine.

PCT/US01/42444

5

10

15

20

25

- 16. The method as set forth in claim 15, wherein the diacylhydrazine is selected from the group consisting of tebufenozide, methoxyfenozide and halofenozide.
- 17. The method as set forth in claim 2, wherein the other insecticide comprises a triazole.
- 18. The method as set forth in claim 17, wherein the triazole comprises triazamate.
- 19. The method as set forth in claim 2, wherein the other insecticide comprises a biological/fermentation product.
- 20. The method as set forth in claim 19, wherein the biological/fermentation product comprises avermeetin or spinosad.
  - 21. The method as set forth in claim 2, wherein the other insecticide comprises a phenyl pyrazone.
  - 22. The method as set forth in claim 21, wherein the phenyl pyrazone comprises fiprinol.
  - 23. The method as set forth in claim 2, wherein the other insecticide comprises an organophosphate.
  - 24. The method as set forth in claim 23, wherein the organophosphate is selected from the group consisting of acephate, fenamiphos, diazinon, chlorpyrifos, chlorpyrifon-methyl and malathion.
  - 25. The method as set forth in claim 2, wherein the other insecticide comprises a carbamate.
  - 26. The method as set forth in claim 25, wherein the carbamate is selected from carbaryl, aldicarb, carbofuran, thiodicarb and oxamyl.
  - 27. The method as set forth in claim 2, wherein the composition is included in a seed coating.
  - 28. The method as set forth in claim 2, wherein at least one of the pyrethroid and the other insecticide is a systemic insecticide.
  - 29. The method as set forth in claim 2, wherein the seed is treated with the composition of the pyrethroid and the other insecticide in an amount effective to provide protection to the seed and/or the shoots and foliage of the plant against damage by the pest.

10

15

20

25

- 30. The method as set forth in claim 2, wherein the seed is treated with the pyrethroid at the same time that it is treated with the other insecticide.
- 31. The method as set forth in claim 2. wherein the seed is treated with the pyrethroid as a different time than it is treated with the other insecticide.
- 32. The method as set forth in claim 29, wherein the composition is included in a seed coating.
- 33. A seed that has been treated with the method as set forth in claim 1.
- 34. The seed as set forth in claim 33, wherein the seed is selected from the group consisting of corn, soybean, cotton, rice, sorghum, sugar beet, wheat, barley, rye, sunflower, tomato, sugarcane, tobacco, rape and oats.
- 35. The seed as set forth in claim 34, wherein the seed is selected from the group consisting of corn, soybean and cotton seed.
- 36. The seed as set forth in claim 35, wherein the seed is corn seed.
- 37. The seed as set forth in claim 33, wherein the seed is a transgenic seed.
- 38. The seed as set forth in claim 37, wherein the transgenic seed is a transgenic corn seed containing a heterologous *Bacillus* thuringiensis gene.
- 39. The seed as set forth in claim 38, wherein the heterologous *Bacillus thuringiensis* gene is one that encodes for the production of a modified Cry3Bb delta-endoxin.
- 40. A composition for the treatment of unsown seed comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.

10

15

20

25

- 41. The composition as set forth in claim 40, wherein the at least one other insecticide is an oxadizine derivative, and the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin.
- 42. A method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating the unsown seed with a composition comprising a nitroguanidine and at least one other insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.
- 43. A seed that has been treated by the method as set forth in claim 42.
- 44. The seed as set forth in claim 43, wherein the seed is selected from the group consisting of corn, soybean, cotton, rice, sorghum, sugar beet, wheat, barley, rye, sunflower, tomato, sugarcane, tobacco, rape and oats.
- 45. The seed as set forth in claim 44, wherein the seed is corn seed.
- 46. The seed as set forth in claim 43, wherein the seed is a transgenic seed.
- 47. A composition for seed treatment prior to sowing comprising a nitroguanidine and at least one other insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.
- 48. A seed that is protected against multiple pests comprising a seed having at least one heterologous gene encoding for the expression of a protein that is active against a first pest and, in addition, having adhered thereto a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide

10

15

20

25

30

selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate, where the composition is present in an amount effective to provide protection to the shoots and foliage of the plant against damage by at least one second pest.

- 49. The seed as set forth in claim 48, wherein the at least one heterologous gene encodes for the expression of a protein that is insecticidally active.
- 50. The seed as set forth in claim 49, wherein the gene is one originally derived from a microorganism selected from the group consisting of *Bacillus*, *Rhizobium*, *Pseudomonas*, *Serratia*, *Trichoderma*, *Glomus*, *Gliocladium* and mycorrhizal fungi.
- 51. The seed as set forth in claim 50, wherein the protein is active against corn root worm.
- 52. The seed as set forth in claim 50, wherein the protein is active against european corn borer.
- 53. The seed as set forth in claim 52 wherein the gene is one originally derived from *Bacillus thuringiensis*.
- 54. The seed as set forth in claim 50, wherein the seed is selected from the group consisting of corn, soybean, cotton, rice, sorghum, sugar beet, wheat, barley, rye, sunflower, tomato, sugarcane, tobacco, rape and oats.
- 55. A method for treating an unsown seed to prevent damage by a pest to the seed and/or shoots and foliage of a plant grown from the seed, the method comprising contacting the unsown seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate.

# (19) World Intellectual Property Organization International Bureau





# (43) International Publication Date 11 April 2002 (11.04.2002)

#### **PCT**

# (10) International Publication Number WO 02/028186 A3

- (51) International Patent Classification<sup>7</sup>: A01N 53/00, 51/00 // (A01N 53/00, 61:00, 57:28) (A01N 51/00, 61:00)
- (21) International Application Number: PCT/US01/42444
- (22) International Filing Date: 2 October 2001 (02.10.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/968,175

60/238,485

6 October 2000 (06.10.2000) US 1 October 2001 (01.10.2001) US

- (71) Applicant (for all designated States except US): MON-SANTO TECHNOLOGY, LLC [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ASRAR, Jawed [US/US]; 14949 Royal Brook, Chesterfield, MO 63017 (US). KOHN, Frank, C. [US/US]; 12532 Larkwood Drive, St. Louis, MO 63146 (US).
- (74) Agent: NELSON MULLINS RILEY & SCARBOR-OUGH; Keenan Building, Third Floor, 1330 Lady Street, Columbia, SC 29201 (US).

- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

- with international search report
- (88) Date of publication of the international search report: 13 March 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



(54) Title: SEED TREATMENT WITH COMBINATIONS OF INSECTICIDES

(57) Abstract: A method of preventing damage to the seed and/or shoots and foliage of a plant by a pest includes treating the seed from which the plant grows with a composition that includes a combination of at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate. It is preferred that when the other insecticide is an oxadiazine derivative, the pyrethroid is selected from the group consisting of taufluvalinate, flumethrin, trans-cyfluthrin, kadethrin, bioresmethrin, tetramethrin, phenothrin, empenthrin, cyphenothrin, prallethrin, imiprothrin, allethrin and bioallethrin. The treatment is applied to the unsown seed. In another embodiment, the seed is a transgenic seed having at least one heterologous gene encoding for the expression of a protein having pesticidal activity against a first pest and the composition has activity against at least one second pest. Treated seeds are also provided.

WO 02/028186 A3

Intern: Application No PCT/US 01/42444

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A01N53/00 A01N51/00 61:00) According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 AO1N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data . \* C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Citation of document, with indication, where appropriate, of the relevant passages Category \* EP 1 013 170 A (AVENTIS CROPSCIENCE SA) 1,3,4, 21,22, 28 June 2000 (2000-06-28) 27-41, 48-55 page 2, line 19 -page 3, line 5 page 3, line 32 - line 44 page 4; example 1 claim 1 X DATABASE WPI 1,2,23, 27-41, Section Ch, Week 199011 Derwent Publications Ltd., London, GB; 48-55 Class CO3, AN 1990-082424 XP002195625 & SU 1 486 135 A (ZERNOPRODUCT GRAIN), 15 June 1989 (1989-06-15) abstract Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the International "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the International filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 2 8: 08. 2002 18 July 2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlean 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Lamers, W Fax: (+31-70) 340-3016

Intern: Application No PCT/US 01/42444

X W. SCHÖBERLEIN ET AL.: "Influence of combined function of the relevant passages and yield after early and normal sowing date" PFLANZENSCHUTZ-NACHRICHTEN BAYER, vol. 52, no. 3, 1999, pages 310-336, XP002195616 page 310, column 2 page 314; table 2  X DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, CHEMICAL CHEMICAL ABSTRACTS SERVICE, COLUMBUS, CHEMICAL CHEMICA			PCT/us 01/42444
X W.SCHÖBERLEIN ET AL.: "Influence of combined fungicide-insecticide treatment of winter wheat seed on crop development and yield after early and normal sowing date"  PFLANZENSCHUTZ-NACHRICHTEN BAYER, vol. 52, no. 3, 1999, pages 310-336, XP002195616  page 310, column 2' page 314; table 2  X DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from STN-INTERNATIONAL, accession no. 124:48362 CA XP002195617' abstract & CN 1 104 033 A (PEOP.REP.CHINA) 28 June 1995 (1995-06-28)  X WO 99 63829 A (HOECHST SCHERING AGREVO GMBH) 16 December 1999 (1999-12-16) page 1, paragraph 2 page 2, paragraph 3 -page 16, paragraph 1 page 16, paragraph 2 page 17, paragraph 4 page 95, paragraph 3  X DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; O.J.SMIDERLE ET AL.: "insecticide treatment and seed quality of corn during storage" retrieved from STN-INTERNATIONAL, accession no. 132:250219 CA XP002195618 abstract & SCI.AGRIC., vol. 56, no. 4, supl., 1999, pages 1245-1254,			
combined fungicide—insecticide treatment of winter wheat seed on crop development and yield after early and normal sowing date" PFLANZENSCHUTZ—NACHRICHTEN BAYER, vol. 52, no. 3, 1999, pages 310-336, XP002195616 page 310, column 2 page 314; table 2  X DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from STN—INTERNATIONAL, accession no. 124:48362 CA XP002195617 abstract & CN 1 104 033 A (PEOP.REP.CHINA) 28 June 1995 (1995-06-28)  X WO 99 63829 A (HOECHST SCHERING AGREVO GMBH) 16 December 1999 (1999-12-16) page 1, paragraph 2 page 2, paragraph 3 -page 16; paragraph 1 page 16, paragraph 5 page 17, paragraph 4 page 95, paragraph 3  X DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; O.J. SMIDERLE ET AL.: "insecticide treatment and seed quality of corn during storage" retrieved from STN—INTERNATIONAL, accession no. 132:250219 CA XP002195618 abstract & SCI. AGRIC., vol. 56, no. 4, supl., 1999, pages	Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
DATABASE CA 'Online'	X	combined fungicide—insecticide treatment of winter wheat seed on crop development and yield after early and normal sowing date" PFLANZENSCHUTZ—NACHRICHTEN BAYER, vol. 52, no. 3, 1999, pages 310-336, XP002195616 page 310, column 2	27-41,
GMBH) 16 December 1999 (1999-12-16) page 1, paragraph 2 page 2, paragraph 3 -page 16, paragraph 1 page 16, paragraph 4 page 95, paragraph 3  DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; O.J.SMIDERLE ET AL.: "insecticide treatment and seed quality of corn during storage" retrieved from STN-INTERNATIONAL, accession no. 132:250219 CA XP002195618 abstract & SCI.AGRIC., vol. 56, no. 4, supl., 1999, pages 1245-1254, ——	<b>X</b> .	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from STN-INTERNATIONAL, accession no. 124:48362 CA XP002195617 abstract & CN 1 104 033 A (PEOP.REP.CHINA)	24, 27-41,
CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; O.J.SMIDERLE ET AL.: "insecticide treatment and seed quality of corn during storage" retrieved from STN-INTERNATIONAL, accession no. 132:250219 CA XP002195618 abstract & SCI.AGRIC., vol. 56, no. 4, supl., 1999, pages 1245-1254,	X	GMBH) 16 December 1999 (1999-12-16)  page 1, paragraph 2  page 2, paragraph 3 -page 16, paragraph 1  page 16, paragraph 5  page 17, paragraph 4	
	X	CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; O.J.SMIDERLE ET AL.: "insecticide treatment and seed quality of corn during storage" retrieved from STN-INTERNATIONAL, accession no. 132:250219 CA XP002195618 abstract & SCI.AGRIC., vol. 56, no. 4, supl., 1999, pages 1245-1254,	24, 27-41,

Intern Application No PCT/US 01/42444

C.(Continu	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	<del></del>
Category.°		Relevant to claim No.
X	DATABASE CA 'Online! 'CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; F.H.ARTHUR: "Residual efficacy of cyfluthrin applied alone or in combination with piperonyl butoxide or piperonyl butoxide + chlorpyrifos-methyl as protectants on stored corn" retrieved from STN-INTERNATIONAL, accession no. 121:101918 CA	1,3,4, 23,24, 27-41, 48-55
. '	XP002195619 abstract & J. ENTOMOL. SCI., vol. 29, no. 2, 1994, pages 276-287,	
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; J. KOSITORNA: "Evaluation of the suitability of the seed insecticidal preparation Montur 190 FS for protection of a sugar beet plantation" retrieved from STN-INTERNATIONAL, accession no. 134:158818 CA XP002195620 abstract & GAZETA CUKROWNICZA, vol. 108, no. 10, 2000, pages 189-191,	1,3,4,7, 8,27-41, 48-55
X .	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; W.HRUBESCH ET AL.: "Insecticides for seed treatment" retrieved from STN-INTERNATIONAL, accession no. 109:2409 CA XP002195621 abstract & ZUCKERINDUSTRIE, vol. 112, no. 12, 1987, pages 1064-1068,	1,3, 25-41, 48-55
X	WO 00 35277 A (NOVARTIS ERFIND VERWALT GMBH; NOVARTIS AG (CH)) 22 June 2000 (2000-06-22) page 7, line 1 - line 11	1-6, 27-41, 48-55
Υ		37–39
Y	WO 99 35913 A (NOVARTIS ERFIND VERWALT GMBH; NOVARTIS AG (CH); SUTTER MARIUS (CH)) 22 July 1999 (1999-07-22) page 1, paragraph 1 -page 83	37-39,46
	-/	

Interi Application No PCT/US 01/42444

- 15		PCT/US 01/42444
	etion) DOCUMENTS CONSIDERED TO BE RELEVANT	· · · · · · · · · · · · · · · · · · ·
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<b>X</b>	WO 97 22254 A (CIBA GEIGY AG; ELMSHEUSER HANS (DE)) 26 June 1997 (1997-06-26)  page 2, paragraph 2 page 4, line 6 - line 11 page 9, line 16 - line 20 page 11, paragraph 15 -page 15, paragraph 1 page 19, line 3 page 19, line 19 - line 22	1-6, 27-45, 47-55
X	page 22, paragraph 3  WO 97 40691 A (CIBA GEIGY AG ;SENN ROBERT (CH); WYSS PETER (CH); MAIENFISCH PETER) 6 November 1997 (1997-11-06) page 1, paragraph 3, page 2, line 1 - line 18 page 9, paragraph 3	1-6, 27-45, 47-55
X	page 10, paragraph 1 - paragraph 3 page 18, paragraph 4 page 2 WO 97 40692 A (CIBA GEIGY AG;;SENN ROBERT	1-6
٨	(CH); WYSS PETER (CH); MAIENFISCH PETER) 6 November 1997 (1997-11-06) cited in the application page 1, paragraph 3 -page 4, line 3 page 22, paragraph 4 page 23, paragraph 3	1-6, 27-45, 47-55
Ρ,Χ	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; A.M.DEWAR ET AL.: "Novel seed tretments to control aphids and virus yellows in sugar beet" retrieved from STN-INTERNATIONAL, accession no. 134:349380 CA XP002195622 abstract & BCPC SYMPOSIUM PROCEEDINGS (2001), 76 (SEED TREATMENT), pages 33-40,	1-6, 27-41, 48-55
	-/	

Interna Application No PCT/US 01/42444

	·	PCI/US 01	/ 42444
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category, °	Citation of document, with indication where appropriate, of the relevant passages	•	Relevant to dalm No.
P,X	DATABASE CA 'Online! 'CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; A.M.DEWAR ET AL.: "Novel seed treatments to control soil pests of sugar beet" retrieved from STN-INTERNATIONAL, accession no. 134:127255 CA XP002195623		1-6, 27-41, 48-55
	abstract & BCPC CONFERENCEPESTS & DISEASES, vol. 3, 13 - 16 November 2000, pages 907-912,	(18004-0	
P,X . '	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; P.A.BIRCH ET AL.: "A new insecticidal seed treatment for oilseed rape" retrieved from STN-INTERNATIONAL, accession no. 134:349379 CA XP002195624 abstract & BCPC SYMPOSIUM PROCEEDINGS (2001), 76 (SEED TREATMENT), pages 27-32,		1,3,4,7, 8,27-41, 48-55
P,X	WO 01 08490 A (MONSANTO CO ;KOHN FRANK (US)) 8 February 2001 (2001-02-08) page 1, line 5 - line 8 page 4, line 23 - line 26 page 9, line 3 - line 28		1-41, 48-55
A .	WO 96 23411 A (RHONE POULENC AGROCHIMIE; MEUNIER LUCIEN (CI); CARUHEL PASCAL (FR)) 8 August 1996 (1996-08-08) page 1, line 5 - line 13 page 2, line 15 - line 16 page 2, line 27 - line 30 page 4, line 5-19 page 4 -page 5; example 1		1-41, 48-55
A	EP 0 194 566 A (AMERICAN CYANAMID CO) 17 September 1986 (1986-09-17) page 1, line 14 - line 16 page 2, line 17 - line 23 page 3, line 1 - line 8		1-41, 48-55
X	DE 198 57 967 A (BAYER AG) 21 June 2000 (2000-06-21) page 2, line 8 -page 3, line 10 page 3, line 25 - line 35 page 3, line 50 -page 4, line 5 page 7, line 20 - line 23 page 7, line 64 - line 65		42-45,47
Υ	-/		46

Interns pplication No PCT/US 01/42444

		PCT/US 01/42444 /
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	Relevant to claim No.
Category °	Citation of document, with Indication, where appropriate, of the relevant passages	Helevant to Gain No.
X	DATABASE CROPU 'Online! A.W.SCHAAFSMA: "Control of seed corn maggot with seed treatments" retrieved from STN-INTERNATIONAL Database accession no. 2000-91026 CROPU XP002206730 abstract & PEST MANAGE.RES.REP., 1999, pages 155-158,	42-45,47
X	FR 2 729 825 A (RHONE POULENC AGROCHIMIE) 2 August 1996 (1996-08-02) page 1, line 5 - line 18	42-45,47
x '	DE 198 23 396 A (BAYER AG) 2 December 1999 (1999-12-02) page 2, line 10 - line 14 page 6, line 52 -page 12, line 39 page 17, line 55	42-45,47
А	DATABASE CROPU 'Online! H.UNEME ET AL.: "Synthesis and insecticidal activity of nitroguanidine derivatives" retrieved from STN-INTERNATIONAL Database accession no. 1999-81777 CROPU XP002206731 abstract & PESTIC.SCI., vol. 55, no. 2, 1999, pages 202-205,	42-47
A	WO 00 28825 A (NOVARTIS ERFIND VERWALT GMBH; SCHNEIDERSMANN FERDINAND MARTI (CA);) 25 May 2000 (2000-05-25) page 1, paragraph 1 page 1, paragraph 3 -page 2, paragraph 1 page 2, paragraph 5 -page 3, paragraph 1 page 5, paragraph 1 page 8, paragraph 2 - paragraph 3 page 13, paragraph 5 -page 13, paragraph 1 page 15, paragraph 2 - paragraph 4	42-47

### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-41, 48-55

A method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating an unsown seed with a composition comprising at least one pyrethrin or synthetic pyrethroid and at least one other insecticide selected from the group consisting of an oxadiazine derivative, a chloronicotinyl, a nitroguanidine, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate,

seeds as described in claims 33-39 and 48-54,
compositions as described in claims 40 and 41 and

\* a method as decribed in claim 55.

#### 2. Claims: 42-47

A method for preventing damage by a pest to a seed and/or shoots and foliage of a plant grown from the seed, the method comprising treating the unsown seed with a composition comprising a nitroguanidine and at least one other insecticide selected from the group consisting of a chloronicotinyl, a pyrrol, a pyrazone, a diacylhydrazine, a triazole, a biological/fermentation product, a phenyl pyrazole, an organophosphate and a carbamate,

\* seeds as described in claims 43-46 and

\* compositions as described in claim 47.

inal application No.

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.:     because they relate to subject matter not required to be searched by this Authority, namely:
Claims Nos.:     because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of Invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
see additional sheet
1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  X No protest accompanied the payment of additional search fees.

Interr plication No PCT/US 01/42444

			1		
Patent document cited in search report		Publication , date	· · ·	Patent family member(s)	Publication date
EP 1013170	·Ą	28-06-2000	EP '	1013170 A1	28-06-2000
SU 1486135	Α .	15-06-1989	ˈˌSU ''	,1486135 ; <b>A</b> 1	15-06-1989
CN 1104033	A .	28-06-1995	NONE		
WO 9963829	A	16-12-1999	DE AU	19825333 A1 4372699 A	09-12-1999 30-12-1999
			BR, WO	9911616 A 9963829 A2	06-'02-2001 16-12-1999
			EP US	1083795 A2 6331531 B1	21-03-2001 18-12-2001
WO 0035277	Á	22-06-2000	WO	0035277 A1	22-06-2000
		•	ΑU	- 2613099 A	03-07-2000
			BR CZ	9816102 A 20012096 A3	04-09-2001 12-12-2001
			FP '	1139738 A1	10-10-2001
WO 9935913	Α,	22-07-1999	AU	744003 B2	14-02-2002
	Ĺ	1.	AU DD	2517699 A 19907010 A	02-08-1999 17-10-2000
			BR +	2317050 A1	22-07-1999
			CN,	1291076 T	11-04-2001
		'	DE	19982477 TO	30-11-2000
•			WO	9935913 A1	22-07-1999
			FR	2773672 A1	23-07-1999
			GB	2349088 A	25-10-2000
			GR	98100481 A	30-11-1999
			HU IT	0100528 A2 MI990051 A1	28-06-2001 14-07-2000
			ĴP	2002509865 T	02-04-2002
			ŇĹ	1011057 C2	22-11-1999
			NL	1011057 A1	19-07-1999
			TR	200001958 T2	21-12-2000
	-, <del></del>		ZA	9900276 A 	16-07-1999
WO 9722254	Ά	26-06-1997	CH	690561 A5	31-10-2000 14-07-1997
	•		AU Ca	1191897 A 2240738 A1	26-06-1997
	1		MO	9722254 A1	26-06-1997
			EP	0883345 Al	16-12-1998
			ZA	9610577 A	18-06-1997 
WO 9740691	A	06-11-1997	UA UA	717868 B2 2387797 A	06-04-2000 19-11-1997
			BR	9709187 A	10-08-1999
			CA	2251877 A1	06-11-1997
			CN	1216900 A	19-05-1999
			EG	21511 A	28-11-2001
			WO	9740691 A1	06-11-1997
			EP JP	0915656 A1 2000509051 T	19-05-1999 18-07-2000
			TR	9802183 T2	21-06-2002
ن من نور نور او الله الله الله و الله من من الله الله الله الله الله الله الله الل			ZÄ	9703629 A	29-10-1997
WO 9740692	A	06-11-1997	AU	718566 B2	13-04-2000
			AU	2699297 A	19-11-1997

Intern Application No
PCT/US 01/42444

çite	D-44 -la a					
WC	Patent document ed in search report		Publication.! date : ' '		Patent family member(s)	Publication , date
***	9740692	ļΑ		BR.	9709181 A	03-08-1999
	J 774003E	,**		CA	2251914 A1	06-11-1997
				CN	1220578 A	23-06-1999
				. WO	9740692 A1	06-11-1997
				EP	0900024 A1	10-03-1999
				JP	2000509379 T	25-07-2000
				TR	9802184 T2	21-06-2002
			- Ca 400 - 200 - La	ZA	9703630 A	29–10–1997 
Mo	0 0108490	Α	08-02-2001	· AU	6492000 A	19-02-2001
,	'			BR	. 0012781 A	07-05-2002
				EP	1198173 A1	24-04-2002
				WO	0108490 A1	08-02-2001
. W(	0 9623411	A	08-08-1996	FR	2729824 A1	02-08-1996
***	0 3023411	, ,,	00 00 1330	FR	2729825 A1	02-08-1996
				AT	191612 T	15-04-2000
				AU	712368 B2	04-11-1999
				AU	4626996 A	21-08-1996
				BR	9607096 A	11-11-1997
				CA	2211105 A1	08-08-1996
				CN	1169656 A ,B	07-01-1998
				CZ	9702410 A3	12 <b>-</b> 11 <b>-1997</b>
				DE	69607743 D1	18-05-2000
				DE	69607743 T2	07-09-2000
				DK	806895 T3	17-07-2000
				EG	21471 A	28-11-2001
				EP	0806895 A1	19-11-1997
				ËS	2144724 T3	16-06-2000
					9623411 A1	08-08-1996
				WO		
				GR	3033227 T3	31-08-2000
				ΗU	9801279 A2	28-08-1998
				ΙL	116947 A	29-06-2000
				JP	10513169 T	15-12-1998'
				PL	321566 A1	08-12-1997
				PT	806895 T	31-08-2000
				RO	116990 B1	28-09-2001
				RU	2159039 C2	20-11-2000
	•			SK	103297 A3	10-12-1997
				TR	9700712 T1	21-01-1998
				US	6077860 A	20-06-2000
				US	5952358 A	14-09-1999
_			<del></del>	_ZA 	9600692 A	19-08-1996
_	P 0194566	Α	17-09-1986	CA	1251727 A1	28-03-1989
E.				EP	0194566 A1	17-09-1986
E.				ES	552779 DO	16-10-1987
Ł.						
E.					8708180 A1	16-12-1987
Ł				ΕŞ		16-12-1987 08-07-1986
Ł				EŞ GR	860660 A1	08-07-1986
Ł				ΕŞ		
			21 06 2000	EŞ GR US ZA	860660 A1 4695564 A 8601727 A	08-07-1986 22-09-1987 26-11-1986
	E 19857967	A	21-06-2000	EŞ GR US ZA DE	860660 A1 4695564 A 8601727 A 19857967 A1	08-07-1986 22-09-1987 26-11-1986 21-06-2000
	E 19857967	A	21-06-2000	EŞ GR US ZA DE AU	860660 A1 4695564 A 8601727 A 19857967 A1 1969800 A	08-07-1986 22-09-1987 26-11-1986  21-06-2000 03-07-2000
	E 19857967	Α	21-06-2000	EŞ GR US ZA DE	860660 A1 4695564 A 8601727 A 19857967 A1	08-07-1986 22-09-1987 26-11-1986 21-06-2000
 Di	E 19857967  R 2729825	AA	21-06-2000	EŞ GR US ZA DE AU	860660 A1 4695564 A 8601727 A 19857967 A1 1969800 A	08-07-1986 22-09-1987 26-11-1986  21-06-2000 03-07-2000

Inter Application No PCT/US 01/42444

Patent document cited in search report		Publication date	1	Patent family member(s)	Publication date
FR 2729825	Ą		AT	191612 T	15-04-2000
111 2723020	77		AÜ	712368 B2	04-11-1999
			AU'	4626996; A	21-08-1996
•			BR	9607096 A	11-11-1997
			· CA'	2211105 A1	08-08-1996
			CN	1169656 A ,B	07-01-1998
			CZ	. 9702410 A3	12-11-1997
			DE.	69607743 D1	18-05-2000
			DE.	69607743 T2	07-09-2000
			DK	∙ 806895 ,T3	17-07-2000
	100		ΈP	0806895 A1	19-11-1997
			ES	2144724 T3	16-06-2000
			·WO	9623411 A1	08-08-1996
			GR	3033227 T3	31-08-2000
			HU	9801279 A2	28-08-1998
			JP	10513169 T	15-12-1998
			PL	321566 A1	08-12-1997
			PT ·	806895 T	31-08-2000
			RO	116990 B1	28-09-2001
			RU	2159039 C2	20-11-2000
			SK	103297 A3	10-12-1997
			TR	9700712 T1	21-01-1998
			US,	6077860 A	20-06-2000
			US	5952358 A	14-09-1999
			EG	21471 A	28-11-2001
			ĪĹ	116947 A	29-06-2000
			ŽĀ	9600692 A	19-08-1996
				9000092 K	
DE 19823396	Α	02-12-1999	DE	19823396 A1	02-12-1999
			AU	4263499 A	13-12-1999
			BR	9910699 A	09-01-2001
			CN	1311632 T	05-09-2001
			WO	9960857 A1	02-12-1999
			ËP	1082014 A1	14-03-2001
			ĴΡ	2002516258 T	04-06-2002
		i	TW	402484 B	21-08-2000
	<b></b> .				
WO 0028825	A	25-05-2000	AU	1651600 A	05-06-2000
			BR	9915398 A	07-08-2001
			CN	1326319 T	12-12-2001
			MO	0028825 A1	25-05-2000
			EP	1130968 A1	12-09-2001